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(54) Title: FUNGICIDAL 1,3,4-OXADIAZINES AND 1,3,4-THIADIAZINES

(57) Abstract

Fungicidal 1,3,4-oxadiazines and 1,3,4-thiadiazines of general formula (I) are disclosed, wherein G<sup>1</sup> is -CR<sup>1</sup>R<sup>7</sup>-, -(CHR<sup>1</sup>CHR<sup>2</sup>C+RR<sup>3</sup>)-, or -(CHR<sup>1</sup>CHR<sup>2</sup>CHR<sup>3</sup>CHR<sup>4</sup>)-; G<sup>2</sup> is -O-, -S-, -S(O)-, -S(O)-, or -NR<sup>27</sup>-; G<sup>3</sup> is -CR<sup>4</sup>R<sup>8</sup>-, -(CHR<sup>5</sup>CHR<sup>6</sup>)-, or -(CHR<sup>3</sup>CHR<sup>5</sup>CHR<sup>6</sup>)- or a direct bond; X is N or CR<sup>13</sup>; Y is N or CR<sup>13</sup>; and E, R<sup>9</sup>, and R<sup>10</sup> are various groups.

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#### TITLE

FUNGICIDAL 1,3,4-OXADIAZINES AND 1,3,4-THIADIAZINES

This invention relates to heterocyclic thiadiazines and related heterocycles useful as agricultural fungicides and compositions containing them.

# BACKGROUND OF THE INVENTION

U.S.S.R. patent 461,929 generically discloses oxadiazines of Formula i and ii

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#### wherein:

R<sup>1</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup>, and R<sup>6</sup> are hydrogen, alkyls, carboxyalkyls, aminoalkyls, phenyl, substituted phenyls, pyridyls, quinolyls, furyls, or thienyls, and

 $\mathbb{R}^2$  is alkyl, substituted alkyl, phenyl, substituted phenyl, or heteroaryl.

U.S.S.R. 461,929 does not specifically name any of the compounds of the instant invention, nor is any utility for the compounds disclosed, in this patent.

# SUMMARY OF THE INVENTION:

This invention pertains to compounds of Formulae I,

25 II, III and IV including all geometric and stereoisomers, agriculturally-suitable salts thereof,
agriculturally-suitable metal complexes thereof,
compositions containing them and their use as
fungicides.

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5 wherein:

-G1-G2-G3- taken together with the attached atoms form a 5-8 membered ring, wherein  $-G^{1}$  is  $-CR^{1}R^{7}$ -;  $-(CHR^{1}CHR^{2})$ -;  $-(CHR^{1}CHR^{2}CHR^{3})$ -; or -(CHR1CHR2CHR3CHR4)-;  $-G^2$  is -O; -S; -S(0)-; -S(0)<sub>2</sub>- or  $-NR^{27}$ -; 10  $-G^3$ - is  $-CR^4R^8$ ;  $-(CHR^5CHR^6)$ -;  $-(CHR^3CHR^5CHR^6)$ - or a direct bond: For example, -G1-G2-G3- can be  $-CHR^{1}CHR^{2}-S-CR^{4}R^{8}-$ , wherein  $-G^{1}-$  is -(CHR<sup>1</sup>CHR<sup>2</sup>)-, - $G^2$ - is -S-, and - $G^3$ - is -CR<sup>4</sup>R<sup>8</sup>-. 15 The directionality of the  $-G^1-G^2-G^3-$  linkage is defined as  $-G^1-G^2-G^3$  in compounds of Formulae I and III and  $-G^3-G^2-G^1$  in compounds of Formulae II and IV. Therefore, for example, when  $-G^{1}$  is  $-(CHR^{1}CHR^{2})$  in a compound of 20 Formula I or III, then the carbon of the CHR<sup>2</sup>.

unit of  $-G^{1}$  is bonded to  $-G^{2}$ . In a compound

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of Formula II or IV, when  $-G^{1}$  is  $-(CHR^{1}CHR^{2})$ , the carbon of the  $CHR^{1}$  unit is bonded to  $-G^{2}$ .

X is N or CR13;

Y is N or CR14;

- E is H; C<sub>1</sub>-C<sub>6</sub> alkyl; C<sub>3</sub>-C<sub>7</sub> cycloalkyl optionally substituted with 1-2 methyl; C<sub>1</sub>-C<sub>6</sub> haloalkyl; C<sub>1</sub>-C<sub>6</sub> alkylthio; C<sub>1</sub>-C<sub>6</sub> alkoxy; C<sub>1</sub>-C<sub>6</sub> haloalkoxy; or phenyl, phenoxy, phenylthio, phenylamino, phenylmethyl, indanyl, tetrahydronaphthalenyl, 1-naphthalenyl, 2-naphthalenyl, thienyl, furanyl or pyridyl each optionally substituted with R<sup>11</sup>, R<sup>12</sup> and R<sup>28</sup>;
  - R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup> and R<sup>8</sup> are each independently H; C<sub>1</sub>-C<sub>4</sub> alkyl; C<sub>1</sub>-C<sub>4</sub> haloalkyl, halogen, CO<sub>2</sub>CH<sub>3</sub>, CO<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>, cyano or phenyl optionally substituted with R<sup>25</sup>;

# provided that

- (i) when  $-G^{1-} = -CR^{1}R^{7-}$  and  $-G^{3-} = -CR^{4}R^{8-}$ , then at least one of  $R^{1}$ ,  $R^{4}$ ,  $R^{7}$  and  $R^{8}$  is hydrogen; in other words the maximum number of carbon atoms in  $-G^{1-}G^{2-}G^{3-}$  with geminal disubstitution is one;
- (ii) the maximum number of optionally substituted phenyl substituents on  $-G^1-G^2-G^3$  is one;
- (iii) -G<sup>3</sup>- is other than a direct bond in compounds of Formulae III and IV; and
- (iv)  $-G^2-G^3$  is other than  $-NR^{27}$  in compounds of Formulae I and II;
- R<sup>9</sup>, R<sup>10</sup> and R<sup>13</sup> are each independently H; halogen; cyano; hydroxy; C<sub>1</sub>-C<sub>6</sub> alkyl; C<sub>1</sub>-C<sub>4</sub> haloalkyl; C<sub>1</sub>-C<sub>4</sub> alkylthio; C<sub>1</sub>-C<sub>4</sub> alkylsulfinyl; C<sub>1</sub>-C<sub>4</sub> alkylsulfonyl; C<sub>3</sub>-C<sub>6</sub> cycloalkyl optionally substituted with 1-2 methyl groups; C<sub>1</sub>-C<sub>4</sub> alkoxy; C<sub>1</sub>-C<sub>4</sub> haloalkoxy; C<sub>2</sub>-C<sub>4</sub> alkoxyalkyl; C<sub>2</sub>-C<sub>4</sub> alkenyl; C<sub>2</sub>-C<sub>4</sub> haloalkenyl; C<sub>2</sub>-C<sub>4</sub>

•	alkenyloxy; $C_2-C_4$ alkynyl; $C_2-C_4$ alkynyloxy;
	NR <sup>29</sup> R <sup>30</sup> ; or phenyl or phenoxy optionally
	substituted with R31; or
	$R^9$ and $R^{13}$ , or $R^{10}$ and $R^{13}$ , or $R^9$ and $R^{14}$ can be
5	taken together to form $-(CH_2)_3-$ , $-(CH_2)_4-$ or a
	fused benzene ring optionally substituted with
	R31;
	$R^{11}$ , $R^{12}$ , $R^{21}$ , $R^{24}$ , $R^{26}$ and $R^{31}$ are each
	independently halogen; C <sub>1</sub> -C <sub>4</sub> alkyl; C <sub>1</sub> -C <sub>4</sub>
10	haloalkyl; C <sub>1</sub> -C <sub>4</sub> alkoxy; or C <sub>1</sub> -C <sub>4</sub> haloalkoxy;
:	R <sup>14</sup> is H; halogen; C <sub>1</sub> -C <sub>2</sub> alkyl; or C <sub>1</sub> -C <sub>2</sub> alkoxy;
	$R^{15}$ , $R^{16}$ , $R^{17}$ , $R^{18}$ , $R^{29}$ and $R^{30}$ are each
	independently H or C1-C2 alkyl; or
٠.	$R^{15}$ and $R^{16}$ , or $R^{17}$ and $R^{18}$ , or $R^{29}$ and $R^{30}$ can be
15	taken together along with the nitrogen atom to
	which they are attached to form a
	4-morpholinyl, pyrrolidinyl or piperidinyl
•	ring;
	$R^{20}$ and $R^{27}$ are each independently H; $C_1-C_4$ alkyl;
20	C <sub>1</sub> -C <sub>4</sub> haloalkyl; C <sub>2</sub> -C <sub>5</sub> alkylcarbonyl; phenyl-
	carbonyl optionally substituted with R21; C3-C4
	alkenyl; C3-C4 alkynyl; phenylmethyl optionally
	substituted with $R^{21}$ on the phenyl ring; $C_1-C_4$
	alkylsulfinyl; C1-C4 alkylsulfonyl; phenyl-
25	sulfinyl, phenylsulfonyl or phenoxycarbonyl
	each optionally substituted with R21; C2-C4
:	alkoxycarbonyl; C(=0)NR <sup>22</sup> R <sup>23</sup> ; C(=S)NHR <sup>23</sup> ;
	$P(=S) (C_1-C_4 \text{ alkoxy})_2$ ; $P(=0) (C_1-C_4 \text{ alkoxy})_2$ ; or
	$S(=0)_2NR^{22}R^{23};$
30	$R^{22}$ is H or $C_1-C_3$ alkyl:
•	R <sup>23</sup> is C <sub>1</sub> -C <sub>4</sub> alkyl; or phenyl optionally
•	substituted with R24; or
	$\mathbb{R}^{22}$ and $\mathbb{R}^{23}$ can be taken together along with the
	nitrogen atom to which they are attached to
35·	form a 4-morpholinyl, pyrrolidinyl, piperidinyl
	an inidepolat ripre

 $R^{25}$  is 1-2 halogen;  $C_1$ - $C_4$  alkyl;  $C_1$ - $C_4$  haloalkyl;  $C_1$ - $C_4$  alkoxy;  $C_1$ - $C_4$  haloalkoxy; nitro; cyano or  $C_1$ - $C_4$  alkylthio;

R<sup>28</sup> is halogen; cyano; nitro; hydroxy;

hydroxycarbonyl; C<sub>1</sub>-C<sub>6</sub> alkyl; C<sub>3</sub>-C<sub>6</sub> cycloalkyl;

C<sub>1</sub>-C<sub>6</sub> haloalkyl; C<sub>1</sub>-C<sub>4</sub> alkylthio; C<sub>1</sub>-C<sub>4</sub> alkyl
sulfinyl; C<sub>1</sub>-C<sub>4</sub> alkylsulfonyl; (C<sub>1</sub>-C<sub>4</sub> alkyl)3
silyl; C<sub>2</sub>-C<sub>5</sub> alkylcarbonyl; C<sub>2</sub>-C<sub>4</sub> alkenyl; C<sub>3</sub>-C<sub>4</sub>

alkenyloxy; C<sub>2</sub>-C<sub>4</sub> alkynyl; C<sub>3</sub>-C<sub>4</sub> alkynyloxy;

C<sub>1</sub>-C<sub>4</sub> alkoxy; C<sub>1</sub>-C<sub>4</sub> haloalkoxy; C<sub>2</sub>-C<sub>4</sub> alkoxy
alkyl; C<sub>2</sub>-C<sub>5</sub> alkoxycarbonyl; C<sub>2</sub>-C<sub>4</sub> alkoxy
alkoxy; NR<sup>15</sup>R<sup>16</sup>; C(=O)NR<sup>17</sup>R<sup>18</sup>; or phenyl,

phenoxy or phenylthio each optionally

substituted with R<sup>26</sup>;

# 15 provided that

when E is,  $C_1$ - $C_6$  alkylthio,  $C_1$ - $C_6$  alkoxy,  $C_1$ - $C_6$  haloalkoxy, phenoxy, phenylthio or phenylamino, then E may only substitute compounds of Formula I.

- In the above recitations, the term "alkyl", used either alone or in compound words such as "alkylthio" or "haloalkyl" denotes straight-chain or branched alkyl; e.g., methyl, ethyl, n-propyl, i-propyl, or the different butyl, pentyl or hexyl isomers.
- 25 "Alkenyl" denotes straight-chain or branched
   alkenes; e.g., 1-propenyl, 2-propenyl, 3-propenyl and
   the different butenyl, pentenyl and hexenyl isomers.
   "Alkenyl" also denotes polyenes such as 1,3-hexadiene
   and 2,4,6-heptatriene.
- 30 "Alkenyloxy" denotes straight-chain or branched alkenyloxy moieties. Examples of alkenyloxy include H<sub>2</sub>C=CHCH<sub>2</sub>O, (CH<sub>3</sub>)<sub>2</sub>C=CHCH<sub>2</sub>O, (CH<sub>3</sub>) CH=CHCH<sub>2</sub>O, (CH<sub>3</sub>) CH=C (CH<sub>3</sub>) CH<sub>2</sub>O and CH<sub>2</sub>=CHCH<sub>2</sub>CH<sub>2</sub>O.

"Alkynyl" denotes straight-chain or branched
35 alkynes; e.g., ethynyl, 1-propynyl, 3-propynyl and the
different butynyl, pentynyl and hexynyl isomers.

"Alkynyl" can also denote moieties comprised of multiple triple bonds; e.g., 2,7-octadiyne and 2,5,8-decatriyne.

"Alkynyloxy" denotes straight-chain or branched alkynyloxy moieties. Examples include HC=CCH<sub>2</sub>O, CH<sub>3</sub>C=CCH<sub>2</sub>O and CH<sub>3</sub>C=CCH<sub>2</sub>O.

"Alkylthio" denotes branched or straight-chain alkylthio moieties; e.g. methylthio, ethylthio, and the different propylthio, butylthio, pentylthio and 10 hexylthio isomers.

Examples of "alkylsulfonyl" include  $CH_3SO_2$ ,  $CH_3CH_2SO_2$ ,  $CH_3CH_2CH_2SO_2$ ,  $(CH_3)_2CHSO_2$  and the different butylsulfonyl, pentylsulfonyl and hexylsulfonyl isomers.

"Alkylsulfinyl" denotes both enantiomers of an alkylsulfinyl group. For example, CH<sub>3</sub>SO, CH<sub>3</sub>CH<sub>2</sub>SO, CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>SO, (CH<sub>3</sub>)<sub>2</sub>CHSO and the different butylsulfinyl, pentylsulfinyl and hexylsulfinyl isomers.

"Alkoxy" denotes, for example, methoxy, ethoxy, 20 n-propyloxy, isopropyloxy and the different butoxy, pentoxy and hexyloxy isomers.

"Cycloalkyl" denotes, for example, cyclopropyl, cyclobutyl, cyclopentyl, and cyclohexyl.

The term "halogen", either alone or in compound

25 words such as "haloalkyl", denotes fluorine, chlorine,
bromine or iodine. Further, when used in compound
words such as "haloalkyl", said alkyl may be partially
or fully substituted with halogen atoms which may be
the same or different. Examples of "haloalkyl" include

30 F<sub>3</sub>C, ClCH<sub>2</sub>, CF<sub>3</sub>CH<sub>2</sub> and CF<sub>3</sub>CF<sub>2</sub>. Examples of "halo-

alkenyl" include (Cl)<sub>2</sub>C=CHCH<sub>2</sub> and CF<sub>3</sub>CH<sub>2</sub>CH=CHCH<sub>2</sub>.

Examples of "haloalkynyl" include HC=CCHCl, CF<sub>3</sub>C=C,

CCl<sub>3</sub>C=C and FCH<sub>2</sub>C=CCH<sub>2</sub>. Examples of "haloalkoxy"

include CF<sub>3</sub>O, CCl<sub>3</sub>CH<sub>2</sub>O, CF<sub>2</sub>HCH<sub>2</sub>CH<sub>2</sub>O and CF<sub>3</sub>CH<sub>2</sub>O.

The total number of carbon atoms in a substituent group is indicated by the "Ci-Ci" prefix where i and j

are numbers from 1 to 8. For example, C<sub>1</sub>-C<sub>3</sub> alkyl-sulfonyl designates methylsulfonyl through propyl-sulfonyl; C<sub>2</sub> alkoxyalkoxy designates CH<sub>3</sub>OCH<sub>2</sub>O; C<sub>3</sub> alkoxyalkoxy designates, for example, CH<sub>3</sub>OCH<sub>2</sub>CH<sub>2</sub>O or CH<sub>3</sub>CH<sub>2</sub>OCH<sub>2</sub>O; and C<sub>4</sub> alkoxyalkoxy designates the various isomers of an alkoxy group substituted with a second alkoxy group containing a total of 4 carbon atoms, examples including CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>O, and CH<sub>3</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>O. Examples of "alkoxyalkyl" include CH<sub>3</sub>OCH<sub>2</sub>, CH<sub>3</sub>OCH<sub>2</sub>CH<sub>2</sub>, CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub> and CH<sub>3</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>. Examples of "alkoxycarbonyl" include CH<sub>3</sub>OC(=O), CH<sub>3</sub>CH<sub>2</sub>OC(=O), CH<sub></sub>

Preferred for reasons of greatest fungicidal activity and/or ease of synthesis are

1. Compounds of Formula I wherein:

Y is N;

E is phenyl, indanyl, tetrahydronaphthalenyl, 1-naphthalenyl, thienyl, or pyridyl each optionally substituted with  $R^{11}$ ,  $R^{12}$  and  $R^{28}$ ;

R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup> and R<sup>8</sup> are each independently H or methyl;

R<sup>11</sup> and R<sup>12</sup> are each independently F, Cl, methyl, trifluoromethyl, methoxy or trifluoromethoxy;

 $R^{13}$  is H;

 $R^9$  and  $R^{10}$  are each independently halogen;  $C_1-C_4$  alkyl; cyclopropyl;  $C_1-C_4$  haloalkyl; allyl; or  $C_2-C_3$  alkynyl; or

 ${\bf R}^9$  and  ${\bf R}^{13}$  can be taken together to form a fused benzene ring optionally substituted with  ${\bf R}^{31}$ ;

R<sup>28</sup> is halogen; cyano; C<sub>1</sub>-C<sub>4</sub> alkyl; C<sub>1</sub>-C<sub>4</sub> haloalkyl; allyl; propargyl; C<sub>1</sub>-C<sub>4</sub> alkoxy; C<sub>1</sub>-C<sub>4</sub> haloalkoxy; or phenyl or

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phenoxy each optionally substituted with  $\mathbb{R}^{26}$ ;

- R<sup>31</sup> is halogen; C<sub>1</sub>-C<sub>4</sub> alkyl or C<sub>1</sub>-C<sub>4</sub> haloalkyl;
- and agriculturally-suitable metal complexes thereof.
- 2. Compounds of Formula III wherein:

Y is N

- E is phenyl, indanyl, tetrahydronaphthalenyl, 1-naphthalenyl, thienyl, or pyridyl each optionally substituted with R<sup>11</sup>, R<sup>12</sup> and R<sup>28</sup>;
- R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup> and R<sup>8</sup> are each independently H or methyl;
- R<sup>9</sup> and R<sup>10</sup> are each independently halogen;
  C<sub>1</sub>-C<sub>4</sub> alkyl; cyclopropyl; C<sub>1</sub>-C<sub>4</sub> haloalkyl;
  allyl; or C<sub>2</sub>-C<sub>3</sub> alkynyl; or
- R<sup>9</sup> and R<sup>13</sup> can be taken together to form a fused benzene ring optionally substituted with R<sup>31</sup>;
- R<sup>11</sup> and R<sup>12</sup> are each independently F, Cl, methyl, trifluoromethyl, methoxy or trifluoromethoxy;
- R13 is H:

R<sup>20</sup> is H;

- $R^{27}$  is H;  $C_1-C_4$  alkyl;  $C_2-C_5$  alkoxycarbonyl;  $C_3-C_4$  alkenyl or  $C_3-C_4$  alkynyl;
- R<sup>28</sup> is halogen; cyano; C<sub>1</sub>-C<sub>4</sub> alkyl; C<sub>1</sub>-C<sub>4</sub> haloalkyl; allyl; propargyl; C<sub>1</sub>-C<sub>4</sub> alkoxy; C<sub>1</sub>-C<sub>4</sub> haloalkoxy; or phenyl or phenoxy each optionally substituted with R<sup>26</sup>:
- R<sup>31</sup> is halogen; C<sub>1</sub>-C<sub>4</sub> alkyl or C<sub>1</sub>-C<sub>4</sub> haloalkyl;
- and agriculturally-suitable metal complexes thereof.

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3. Compounds of Preferred 1 wherein:
G<sup>2</sup> is 0; S or NR<sup>27</sup>;
E is phenyl optionally substituted with R<sup>11</sup>,
R<sup>12</sup> and R<sup>28</sup>; indanyl or tetrahydronaphthalenyl; and agriculturally-suitable metal complexes thereof.

4. Compounds of Preferred 3 wherein: G<sup>2</sup> is O; S; NH or N(C<sub>1</sub>-C<sub>4</sub> alkyl); E is phenyl optionally substituted with R<sup>11</sup>, R<sup>12</sup> and R<sup>28</sup>; and agriculturally-suitable metal complexes thereof.

Specifically preferred for greatest fungicidal activity and/or ease of synthesis are:

3-(4,6-dimethyl-2-pyrimidinyl)-3,6-dihydro-5-phenyl-2H-1,3,4-oxadiazine

3-(4,6-dimethyl-2-pyrimidinyl)-5-(4-ethylphenyl)-3,6-dihydro-2H-1,3,4-oxadiazine

20 2-(2-chlorophenyl)-4-(4,6-dimethyl-2-pyrimidinyl)-5,6-dihydro-4H-1,3,4-thiadiazine

4-(4,6-dimethyl-2-pyrimidinyl)-2-(4-ethylphenyl)-5,6-dihydro-4H-1,3,4-thiadiazine

### DETAILED DESCRIPTION OF THE INVENTION

Compounds of Formula I wherein E is as described in the Summary of the Invention except that E is not phenoxy, phenylthio, phenylamino,  $C_1$ - $C_6$  alkoxy,  $C_1$ - $C_6$  alkylthic and  $C_1$ - $C_6$  haloalkoxy can be prepared by one or more of the methods described in Equations 1-6 and 13.

Compounds of Formula 2 in Equation 1 can be prepared by reacting hydrazine 1 with an acid chloride and a base such as pyridine or triethylamine at 0°C in a solvent such as dichloromethane, THF, or pyridine (Equation 1). The hydrazines 1 are known in the

literature (*J. Pest. Sci.*, 1990, 15, 13) and can be prepared by one skilled in the art as taught in EP 293,743-A and by Naito et al. in *Chem. Pharm. Bull.*, 1969, 17, 1467.

# 5 Equation 1

Compounds of Formula 4 can be prepared by treatment

of hydrazides of Formula 2 with P<sub>2</sub>S<sub>5</sub> in pyridine at
reflux for 1-2 h to form thiohydrazides of Formula 3,
followed by reaction with an appropriate alkylating
agent, wherein L can be Cl, Br, I or tosylate, in the
presence of two equivalents of base, such as triethylamine (Equation 2). In some cases, additional base
such as sodium hydride is necessary to induce
cyclization. The cyclization reaction is typically
performed at 25° to 100°C in an inert aprotic solvent
such as THF or acetonitrile.

# 20 Equation 2

Compounds of Formula 5 can be prepared similarly by 25 treatment of hydrazides of Formula 2 with an alkylating

agent and two equivalents of base using the cyclization procedure previously described for the preparation of compounds of Formula 4 (Equation 3).

Equation 3

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Compounds of Formula 7 can be prepared by the reaction of hydrazines of Formula 1 with ketones of

10 Formula 6 in a solvent such as acetonitrile, dichloromethane or acetic acid. The desired heterocycles of Formula 8 can be formed by treatment of the resulting product with a ketone or aldehyde in the presence of a catalytic amount of acid such as butanesulfonic acid

15 (Equation 4). This reaction is typically conducted at 25° to 100°C in an anhydrous organic solvent such as THF or acetonitrile for 12 to 24 h.

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# Equation 4

Compounds of Formula 6 wherein m=1 and Q=0 can be prepared by  $\alpha$ -hydroxylation of a methyl ketone with iodosobenzene as described by Moriarty et al. in Tetrahedron Lett., 1981, 22, 1283.

Thiols of Formula 7b and amines of Formula 7c can be prepared as outlined in Equation 5. Alcohols of Formula 7a (Q=0) can be converted to the corresponding mesylate by methods known in the art. The mesylates can be treated with sodium sulfide to form the thiols 7b, or they can be reacted with potassium phthalimide and then hydrazine to form amines of Formula 7c.

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# Equation 5

Formation of heterocycles of Formula 9 can be accomplished by treatment of hydrazones of Formula 7 with the appropriate alkylating agent as previously described for the preparation of heterocycles of Formula 4 (Equation 6).

# Equation 6

Compounds of Formula I wherein E is phenoxy, phenylthio, phenylamino,  $C_1$ - $C_6$  alkoxy,  $C_1$ - $C_6$  alkylthio or  $C_1$ - $C_6$  haloalkoxy can be prepared by one or more of the methods described in Equations 7-13.

Heterocycles of Formula 11 can be prepared by

treating methylthio-substituted compounds of Formula 10
with various nucleophiles in the presence of a base.
Suitable nucleophiles can be optionally substituted
phenols, thiophenols, or anilines, C<sub>1</sub>-C<sub>6</sub> alkylthiols,
C<sub>1</sub>-C<sub>6</sub> alcohols and C<sub>1</sub>-C<sub>6</sub> halo-substituted alcohols

(Equation 7).

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# Equation 7

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Nu = optionally substituted phenol, thiophenol, or aniline;  $C_1-C_6$  alkylthiol;  $C_1-C_6$  alcohol,  $C_1-C_6$  halo-substituted alcohol

n = 0, 1, 2, 3c

 $Q = 0, S, N-R^{27}$ 

 $R, R^a, R^b = R^1, R^2, R^3, R^4, R^7$ 

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The methythio-substituted heterocycles of Formula 10 can be synthesized by reaction of carbazates of Formula 12 with an alkylating agent in the presence of two equivalents of base, such as triethylamine (Equation 8). This type of cyclization was described previously for the preparation of compounds of Formula 4 (Equation 2). Compounds of Formula 12 are known in the literature and can be prepared by one skilled in the art (e.g., see G. W. Stacy, "Heterocyclic"

20 Compounds, R. C. Elderfield, ed., Wiley, NY, 1961, vol. 7, p 835).

#### Equation 8

5 Alternatively, compounds of Formula 10% can be prepared by sequential treatment of carbazates of Formula 13 with P<sub>2</sub>S<sub>5</sub> and iodomethane in pyridine (Equation 9). Carbazates of Formula 13 are known in the literature (e.g., see Dox, J. Am. Chem. Soc., 1926, 10 48, 1951).

# Equation 9

15

 $R, R^{a}, R^{b}=R^{1}, R^{2}, R^{3}, R^{4}, R^{7}$ 

$$R^9$$
 $X$ 
 $R^{10}$ 
 $R^{2}$ 
 $R$ 

Methylthio-substituted heterocycles of Formula 15 can be prepared by treating hydrazides of Formula 14 with  $P_2S_5$  in pyridine at reflux and then alkylating the resulting thio derivative with iodomethane in the presence of a base such as triethylamine (Equation 10).

Reaction of compounds of Formula 15 with nucleophiles and base, as previously described for the preparation of compounds of Formula 11 in Equation 7, yields products of Formula 16. The seven-membered ring analogs, compounds of Formula 17, can be prepared from hydrazides of Formula 14a by the same procedure (Equation 10).

# Equation 10

10  $m = 1,2,3; Q = 0,S,N-R^{27}; R^c,R^d = R^3,R^4,R^5,R^6,R^8$ 

Q=0, s, NR<sup>27</sup>

Treatment of hydrazides of Formula 19 with an aldehyde or ketone in the presence of a catalytic amount of acid, such as butanesulfonic acid, yields heterocycles of Formula 14 (Equation 11). The cyclization is typically performed at 25° to 100°C in

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an anhydrous organic solvent such as THF or acetonitrile.

#### Equation 11

Compounds of Formula 19a (Q=O) can be synthesized by condensing hydrazine 1 with hydroxyacids of Formula 18 in the presence of a dehydrating agent such as dicyclohexylcarbodiimide in an inert aprotic solvent such as THF or dichloromethane. Hydroxyacids of Formula 18 are well-known to one skilled in the art. Thiols of Formula 19b (Q=S) and amines of Formula 19c (Q=NR<sup>27</sup>) can be prepared by forming the mesylate of 15 alcohols of Formula 19a followed by displacement with nucleophiles in a manner similar to that previously described for the preparation of compounds of Formulae 7b and 7c (Equation 5).

Compounds of 14a can be prepared by treatment of hydrazides of Formula 19d (m=1) with the appropriate alkylating agent, as illustrated in Equation 12, according to procedures described above (see Equations 2 and 3).

#### Equation 12

Compounds of Formula Ib wherein G<sup>2</sup> is S(O) or S(O)<sub>2</sub> can be prepared from the corresponding thio analogue Ia by well-known methods for oxidation of sulfur (Equation 13). Typical reagents for this type of oxidation include m-chloroperoxybenzoic acid, hydrogen peroxide, sodium metaperiodate, and OXONE® (potassium peroxymonosulfate).

# Equation 13

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Compounds of Formula II can be prepared by one or more of the following methods described in Equations 14-19.

Hydrazides of Formula 22 can be synthesized by the 20 reaction of hydrazine 21 with an acid chloride of

Formula 20 in the presence of a base such as triethylamine or pyridine (Equation 14). Typical solvents for this reaction are dichloromethane and THF. Equation 14

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The acid chloride of Formula 20 can be prepared by treatment of the corresponding carboxylic acid with thionyl chloride. Methods for preparing acid chlorides from carboxylic acids are well-known in the literature.

Procedures for preparing pyrimidine carboxylic acids are described by Sakamoto, T., and Yamanaka, H. in Heterocycles, 1981, 15, 583.

15 Heterocycles of Formula 24 can be prepared by treating hydrazides of Formula 22 with P<sub>2</sub>S<sub>5</sub> in pyridine at reflux to form the thiohydrazides of Formula 23, followed by reaction of 23 with an alkylating agent in the presence of two equivalents of base such as 20 triethylamine (Equation 15). Typically, these reactions are conducted at 25° to 100°C in an inert aprotic solvent such as THF or acetonitrile.

#### Equation 15

5 Compounds of Formula 25 can be prepared similarly by treatment of hydrazides of Formula 22 with an alkylating agent and two equivalents of base according to the previously described cyclization procedure (Equation 16).

# 10 Equation 16

Compounds of Formula 28 can be synthesized by the reaction of hydrazines of Formula 21 with ketones of Formula 26 in a solvent such as dichloromethane or acetonitrile to form hydrazones of Formula 27 (Equation 17). The hydrazone can then be treated with a ketone

or aldehyde in the presence of a catalytic amount of acid, such as butanesulfonic acid, to form cycloadducts of Formula 28. This reaction is typically carried out at 25° to 100°C in an anhydrous organic solvent such as THF or acetonitrile.

Equation 17

WO 93/22311

10 Hydroxyketones of Formula 26a (Q=0, m=1) can be prepared by α-hydroxylation of the corresponding methyl ketone 29 with iodosobenzene as described by Moriarty et al. in Tetrahedron Lett., 1981, 22, 1283, and illustrated in Equation 18. Methods to prepare 15 heteroaryl ketones of Formula 29 are well-known in the art. The corresponding thiols of Formula 26b (Q=S) and amines of Formula 26c (Q=NR<sup>27</sup>) can be prepared by methods previously described for thiols and amines of Formulae 7b and 7c, respectively (Equation 5).

#### Equation 18

Compounds of Formula IIb can be synthesized from the corresponding this analogue of Formula IIa by exidation (Equation 19). Typical reagents for this type of exidation include m-chloroperoxy benzoic acid, hydrogen peroxide, sodium metaperiodate, and OXONE® (potassium peroxymonosulfate).

# Equation 19

by reduction of compounds of Formulae I and II, respectively, with sodium borohydride/titanium (IV) chloride according to the procedure taught by Kano et al. in Synthesis, 1980, 695, and set forth in Equation 20. In cases where substituents in compounds of Formulae I and II are not compatible with the reduction conditions, protection and deprotection techniques, which are well-known in the art may be employed.

# Equation 20

Compounds of Formulae IIIa and IVa can be capped on nitrogen with various substituents (R<sup>20</sup>) by treating with the appropriate alkylating, acylating, sulfonylating or phosphonylating agent of Formula 30 as shown in Equation 21. The leaving group (Lg) in compounds of Formula 30 may be CI, Br, I, acetate or other moeity known to act as a leaving group.

Typically, these reactions are run in inert solvents such as THF, benzene or dichloromethane in the presence of a tertiary amine base, such as triethylamine, at a temperature ranging from 0° to 100°C.

# Equation 21 :

Compounds of Formula IIIb and IVb wherein R<sup>20</sup> is C(=0)NR<sup>22</sup>R<sup>23</sup> or C(=S)NHR<sup>23</sup> can be prepared by treating compounds of Formulae IIIa or IVa with an isocyanate or isothiocyanate by methods well-known in the art (Equation 22). Typical solvents for this type of reaction are THF, acetonitrile and dichloromethane.

# Equation 22

IIIa + W=C=N-R<sup>22</sup>

R<sup>20</sup> = H W = O, S

$$R^9$$
 $R^{10}$ 
 $R^{20}$ 
 $R^{20}$ 

Compounds of Formula 3, as illustrated in Equation 2, can also be prepared by reacting hydrazine 1 with the appropriate carboxymethyl dithioate 31 in aqueous sodium hydroxide at 25°C (Equation 23). Carboxymethyl dithioates are known in the literature and can be prepared by one skilled in the art (see Jensen, K. A. and Pedersen, C., Acta Chemica Scandinavica, 1961, 15, 1087).

# 15 Equation 23

Likewise, thiohydrazides of Formula 23, as
20 illustrated in Equation 15, can be synthesized by

reaction of a hydrazine of Formula 21 with a carboxymethyl dithioate of Formula 32 in aqueous sodium hydroxide (Equation 24).

Equation 24

Equation 2

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Compounds of Formula 11, wherein E is phenoxy or phenylthio, can also be synthesized by treating a hydrazine of Formula 1 with phenyl-chlorothionoformate or phenyl-chlorodithioformate of Formula 33 to form a thiocarbazate hydrochloride of Formula 34 (Equation 25). This type of reaction is typically run in a solvent such a methylene chloride from about -10°C to 0°C. The cyclization is performed by treating 39 with the appropriate alkylating agent in a solvent mixture of aqueous sodium hydroxide and THF at 25°C.

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#### Equation 25

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$$\bigcap_{A} \bigcap_{A} \bigcap_{B} \bigcap_{A} \bigcap_{B} \bigcap_{A} \bigcap_{B} \bigcap_{A} \bigcap_{B} \bigcap_{A} \bigcap_{B} \bigcap_{A} \bigcap_{B} \bigcap_{B} \bigcap_{A} \bigcap_{B} \bigcap_{B}$$

n=0,1,2,3 R,R<sup>a</sup>,R<sup>b</sup>=R<sup>1</sup>,R<sup>2</sup>,R<sup>3</sup>,R<sup>4</sup>,R<sup>7</sup> L=C1,Br,I,OTs

The metal complexes of compounds of Formulae I-IV of the instant invention include complexes with copper, zinc, iron, magnesium, or manganese. These complexes can be formed by combining the compound of Formulae I-IV with the metal salt in either aprotic solvents, such as ether or THF; or protic solvents, such as methanol. EP-A-459,662 discloses metal complexes of other nitrogen containing compounds as agricultural fungicides.

# EXAMPLE 1

Preparation of 1-(4-ethylphenyl)-2-hydroxyethanone(4,6-dimethyl-2-pyrimidinyl)hydrazone

To a solution of 3.57 g (21.7 mmol) of p-ethyl-220 hydroxyacetophenone in 100 mL of acetonitrile was added
3.00 g (21.7 mmol) of 4,6-dimethyl-2-hydrazinopyrimi-

dine, 3Å molecular sieves, and a catalytic amount of butanesulfonic acid. The reaction mixture was stirred overnight at room temperature and then diluted with dichloromethane and chloroform. The organic phase was washed successively with saturated sodium bicarbonate and brine, dried over sodium sulfate, filtered and concentrated. The crude product was passed through a plug of silica gel and triturated with hexanes to yield 3.45 g of product. <sup>1</sup>H NMR (CDCl<sub>3</sub>) & 10.65 (bs, 1H), 7.61 (d, 2H), 7.15 (d, 2H), 6.47 (s, 1H), 6.10 (bs, 1H), 4.86 (s, 2H), 2.64 (q, 2H), 2.38 (s, 6H), 1.22 (t, 3H).

#### EXAMPLE 2

# Preparation of 3-(4,6-dimethyl-2-pyrimidinyl)-5-(4-

25 ethylphenyl)-3.6-dihydro-2H-1,3.4-oxadiazine
A solution of 1.00 g (3.52 mmol) of 1-(4-ethyl-phenyl)-2-hydroxyethanone(4,6-dimethyl-2-pyrimidinyl)-hydrazone, 0.21 g (7.04 mmol) of paraformaldehyde, and

- a catalytic amount of butanesulfonic acid was heated at reflux for 3 h in 20 mL of acetonitrile. After cooling, the reaction mixture was diluted with dichloromethane and chloroform. The organic phase was washed successively with saturated sodium bicarbonate and brine, dried over sodium sulfate, filtered and
- 25 concentrated. Chromatography on silica gel gave 70 mg of desired product as a gum. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.66 (d, 2H), 7.21 (d, 2H), 6.56 (s, 1H), 5.54 (s, 2H), 4.81 (s, 2H), 2.67 (q, 2H), 2.42 (s, 6H), 1.24 (t, 3H).

# EXAMPLE: 3

# 30 Preparation of 4-ethylbenzoic acid 2-(4.6-dimethyl-2-pyrimidinyl)hydrazide

4,6-Dimethyl-2-hydrazinopyrimidine (3.72 g, 26.95 mmol) was suspended in 80 mL of pyridine and the reaction mixture was cooled to 10°C. After slowly adding p-ethylbenzoyl chloride (5.00 g, 29.66 mmol), the reaction mixture was allowed to warm to room

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temperature over 1 h. Addition of ice and water precipitated the product which was filtered and washed with hexanes to yield 6.85 g of a white solid. mp 118-119°C. <sup>1</sup>H NMR (CDCl<sub>3</sub>) & 9.15 (bs, 1H), 7.8 (d, 2H), 7.35 (bs, 1H), 7.2 (d, 2H), 6.52 (s, 1H), 2.7 (q, 2H), 2.33 (s, 6H), 1.23 (t, 3H).

#### EXAMPLE 4

# Preparation of 4-(4,6-dimethyl-2-pyrimidinyl)-2-(4-ethylphenyl)-5.6-dihydro-4H-1,3,4-thiadiazine

A solution of 5.30 g (18.52 mmol) of 4-ethylbenzoic acid 2-(4,6-dimethyl-2-pyrimidinyl) hydrazide and 6.18 g (13.89 mmol) of P2S5 in 60 mL of pyridine was heated at reflux for 1.5 h. After cooling, water was added and the reaction mixture was heated briefly at reflux to quench the reaction. The mixture was then cooled with an ice bath to precipitate the product. The solid was filtered and washed with water to give 6.57 g (21.73 mmol) of thiohydrazide which was then dissolved in 100 mL of THF with 7.5 mL (54.33 mmol) of triethylamine and 2.1 mL (23.91 mmol) of 1,2-dibromoethane. The reaction mixture was heated at reflux overnight. After cooling, water and ether were added and the organic phase was separated and washed with brine. The organic extracts were dried over magnesium sulfate, filtered and concentrated. The crude product was passed through a plug of silica gel to give 200 mg of product as an oil. <sup>1</sup>H NMR (CDCl<sub>3</sub>), 7.8 (d, 2H), 7.2 (d, 2H), 6.53 (s, 1H), 4.45 (m, 2H), 3.35 (m, 2H), 2.67 (q, 2H), 2.41 (s, 6H), 1.22 (t, 3H).

#### EXAMPLE 5

Preparation of 4-(4.6-dimethyl-2-pyrimidinyl)-5.6dihydro-2-(3-methylphenyl)-4H-1.3.4-oxadiazine A solution of 1.00 g (3.89 mmol) of 3-methylbenzoic acid 2-(4,6-dimethyl-2-pyrimidinyl)hydrazide, 0.37 mL

(4.28 mmol) of 1,2-dibromoethane, and 1.33 mL (8.95 mmol) of DBU in 20 mL of dry THF was heated at

reflux overnight. After cooling, 2.3 equivalents (8.95 mmol) of sodium hydride and 0.37 mL (4.28 mmol) of 1,2-dibromoethane were added, and the reaction mixture was heated at reflux overnight. The mixture was allowed to cool to room temperature and saturated aqueous ammonium chloride was added. The product was extracted with dichloromethane and chloroform and the organic phase was washed with brine. The organic extracts were dried over sodium sulfate, filtered, concentrated, and passed through a plug of silica gel to give 100 mg of desired product as a gum. 1H NMR (CDCl<sub>3</sub>) & 7.82 (m, 1H), 7.75 (m, 1H), 7.25 (m, 1H), 7.19 (m, 1H), 6.49 (s, 1H), 4.54 (m, 2H), 4.28 (m, 2H), 2.42 (s, 6H), 2.38 (s, 3H).

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#### . EXAMPLE 6

# Preparation of 4-methoxybenzenecarbothioic acid O-[2-(4,6-dimethyl-2-pyrimidinyl)hydrazide

4,6-Dimethyl-2-hydrazinopyrimidine (p-methoxy-thiobenzoylthio)acetic acid (2.00 g), 14.49 mmol) and p-methoxyphenylcarboxymethyldithioate (3.48 g, 14.4 mmol) were dissolved in 20 mL of 1N aqueous sodium hydroxide and 10 mL of water. The reaction mixture was stirred at 25°C for 16 h and then acidified with 1N HCl. The resultant precipitate was filtered, washed with water, and dried under vacuum to give 3.22 g (11.2 mmol, 78%) of the title hydrazide as a white solid, m.p. 212-215°C <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 9.5 (bs, 1H), 7.85 (d, 2H), 6.95 (d, 2H), 6.57 (s, 1H), 3.87 (s, 3H), 2.39 (s, 6H).

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### EXAMPLE 7

1,2-dibromoethane (0.44 g, 2.33 mmol) were dissolved in

Preparation of 4-(4.6-dimethyl-2-pyrimidinyl)5.6-dihydro-2-phenyl-4H-1.3.4-thiadiazine
Benzenecarbothioic acid O-[2-(4,6-dimethyl-2-pyrimidinyl)]hydrazide (0.500 g, 1.94 mmol),
triethylamine (4.85 mmol, 0.67 mL) and

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10 mL of THF and heated at reflux for 5 h. After cooling, water was added and the mixture was extracted with ethyl acetate. The organic layer was washed with brine, dried over sodium sulfate, filtered and 5 concentrated. The product was purified by flash chromatography on silica gel to yield 0.490 g (1.73 mmol) of a solid in 89% yield, m.p. 138-142°C. 1H NMR (CDCl<sub>3</sub>) δ 7.88 (m, 2H), 7.37 (m, 3H), 6.55 (s, 1H), 4.47 (m, 2H), 3.36 (m, 2H), 2.42 (s, 6H).

#### EXAMPLE 8

Preparation of 4-(4.6-dimethyl-2-pyrimidinyl)-2-(4ethylphenyl)-5,6-dihydro-4H-1,3,4-thiadiazine 1-oxide

4-(4,6-Dimethyl-2-pyrimidinyl)-2-(4-ethylphenyl)-5,6-dihydro-4H-1,3,4-thiadiazine (0.800 g, 2.56 mmol) was dissolved in 10 mL of methanol and 2.5 mL of water. Sodium metaperiodate (0.600 g. 2.82 mmol) was added and the reaction mixture was heated at reflux for 1 h. Ethanol (2.5 mL) was added and heating was continued for 1 h more. The reaction mixture was then stirred at 25°C for 16 h. An additional 200 mg of sodium metaperiodate was added and the mixture was heated at reflux for 1 h. The reaction mixture was washed with water and extracted with methylene chloride. The organic layers were washed with brine, dried over 25 sodium sulfate, and concentrated. The crude product was passed through a plug of silica gel to give 760 mg (91% yield) of a white solid, m.p. 149-164°C. 1H NMR (CDCl<sub>3</sub>)  $\delta$  7.95 (d, 2H), 7.28 (d, 2H), 6.7 (s, 1H), 5.45 (m, 1H), 3.9 (m, 1H), 3.4 (m, 1H), 2.85 (m, 1H), 2.7 (q, 2H), 2.49 (s, 6H), 1.26 (t, 3H).

#### EXAMPLE 9:

Preparation of 4-(4.6-dimethyl-2-pyrimidinyl)-2-(4-ethylphenyl)-5.6-dihydro-4H-1.3.4-thiadiazine 1.1-dioxide

4-(4,6-Dimethyl-2-pyrimidinyl)-2-(4-ethylphenyl)-5,6-dihydro-4H-1,3,4-thiadiazine 1-oxide (0.350 g,

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1.06 mmol) was dissolved in 5 mL of methanol and 2.5 mL of water. The mixture was cooled to 0°C and Oxone® (potassium peroxymonosulfate) (0.490 g, 0.80 mmol) was added. The reaction was warmed to room temperature,
5 stirred for 1 h, then heated at reflux for 10 min. After stirring at 25°C for 16 h, water was added and the reaction mixture was extracted twice with methylene chloride. The combined organic layers were washed with brine, dried over sodium sulfate, and concentrated.
10 The crude product was passed through a plug of silica gel to yield 350 mg (96%) of a white solid, m.p. 139-141°C. ¹H-NMR (CDCl<sub>3</sub>) δ 7.90 (d, 2H), 7.27 (d, 2H), 6.72 (s, 1H), 5.05 (m, 2H), 3.55 (m, 2H), 2.67 (q, 2H), 2.47 (s, 6H), 1.24 (t, 3H).

EXAMPLE 10

Preparation of 4-(4.6-dimethyl-2-pyrimidinyl)-5.6-dihydro-2-phenoxy-4H-1,3.4-thiadiazine

O-Phenyl 2-(4,6-dimethyl-2-pyrimidinyl)hydrazinecarbothicate hydrochloride (4.00 g, 12.74 mmol) was

20 dissolved in 38.5 mL of 1N aqueous sodium hydroxide,
40 mL of THF, and 1.31 mL (15.29 mmol) of
1,2-dibromoethane. The reaction mixture was stirred at
25°C for 4 days. Methylene chloride was added and the
reaction was washed successively with water and brine.

25 After drying over sodium sulfate and concentrating, the
crude product was passed through a plug of silica gel
to give 2.48 g (8.27 mmol, 65%) of a solid, m.p.
75-85°C. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.31 (m, 4H), 7.18 (m, 1H),

The compounds illustrated below are referred to in the tables which follow.  $G^1$ ,  $G^2$ ,  $G^3$ , X, Y, E and  $R^1-R^{28}$  are as defined for compounds of Formulae I-IV in the Summary of the Invention. In addition:

6.47 (s, 1H), 4.39 (m, 2H), 3.29 (m, 2H), 2.36 (s, 6H).

35 n = 0-2, as in the disclosure (e.g., Equation 2);  $n^1 = 1-3$ :  $n^2 = 0-1;$ 

 $\mathrm{MCl}_{\mathbf{x}}$  = the metal chloride salts of copper, zinc, iron, magnesium, or manganese; and

$$x = 1-2.$$

$$\begin{array}{c|c} \text{CH}_3 & \text{CH}_3 \\ & & \\ N & N & R^{11} \\ & & \\ G^Z & & G^{28} \end{array}$$

Ih

Ii.

IIc

$$\begin{array}{c|c} CH_3 & CH_3 \\ \hline R^1 & N & N \\ \hline R^7 & N & N \\ \hline R^5 & R^6 & CH_3 \\ \end{array}$$

Ik

IIIc

IId

ΙΙ£

CH<sub>3</sub>
N
N
CH<sub>3</sub>
R
CH<sub>3</sub>
CH<sub>3</sub>
CH<sub>3</sub>
CH<sub>3</sub>
CH<sub>3</sub>

The following abbreviations are used in the tables which follow. All alkyl groups are the normal isomers unless indicated otherwise.

t - is tertiary

s - is secondary

n - is normal

i - is iso

c - is cyclo

Me - is methyl

Et - is ethyl

Pr - is normal-propyl

Bu - is normal-butyl

Hex - is normal-hexyl

Ph - is phenyl

Bzl - is benzyl

*i*-Pr - is isopropyl

t-Bu - is tertiary-butyl
c-Pr - is cyclopropyl
c-Hex - is cyclohexyl
s-Bu - is secondary-butyl
OMe - is methoxy
i-PrO - is isopropoxy
SEt - is ethylthio
CN - is cyano
TBS - is t-butyldimethylsilyl
Ac - is acetyl
S(O)Me - is methylsulfinyl
S(O)2Me - is methylsulfonyl

Compounds of Formula Id				
G <sup>2</sup> =S, R <sup>9</sup> =Me, Y=N,	OCH2CH=CH2	i-Pr		
X=CH	CH <sub>2</sub> CH <sub>2</sub> OMe	c-Pr		
R <sup>10</sup>	OCHF <sub>2</sub>	c-Hex		
В.	C≡CH	.2-Me-c-Pr		
Cl	C≡CCH <sub>2</sub> CH <sub>3</sub>	CF <sub>3</sub>		
Br	OCH2C=CH	(CH <sub>2</sub> ) <sub>3</sub> CF <sub>3</sub>		
F	NE <sub>2</sub>	SMe		
CN	NMe <sub>2</sub>	SBu		
OH	NHEt	S (0) Me		
Me	4-morpholinyl	S (0) Bu		
Hex	pyrrolidinyl	S (O) 2Me		
Et .	piperidinyl	S (O) 2Bu		
1-Pr	Ph	OMe		
c-Pr	PhO	ÒBu ·		
c-Hex	4-Me-Ph	OCH <sub>2</sub> CF <sub>3</sub>		
2-Me-c-Pr	3-CF <sub>3</sub> -Ph	0 (CH <sub>2</sub> ) 3CF3		
CF3	4-i-Pr-PhO	CH <sub>2</sub> OMe		
(CH <sub>2</sub> ) <sub>3</sub> CF <sub>3</sub>	4-F <sub>2</sub> HCO-Ph	(CH <sub>2</sub> ) 3 <sup>OMe</sup>		
SMe	3-Et-PhO	CH=CHMe		
SBu	4-MeO-PhO	СН=СНСН2СН3		
S (0) Me	4-MeO-Ph	CH=CHCH2CF3		
S (0) Bu	•	CH=CCl <sub>2</sub>		
S(0) <sub>2</sub> Me	G <sup>2</sup> =0, R <sup>9</sup> =Me, Y=N,	OCH2CH=CH2		
S (O) 2Bu	X=CH ·	CH <sub>2</sub> CH <sub>2</sub> OMe		
ОМе	R <sup>10</sup>	OCHF <sub>2</sub>		
OBu	H	C≡CH		
OCH <sub>2</sub> CF <sub>3</sub>	ст	C≡CCH <sub>2</sub> CH <sub>3</sub>		
O(CH <sub>2</sub> ) <sub>3</sub> CF <sub>3</sub>	. Br	OCH <sub>2</sub> C≡CH		
CH <sub>2</sub> OMe	·F	NH <sub>2</sub>		
(CH <sub>2</sub> ) 30Me	CN	NMe <sub>2</sub>		
CH=CHMe	OH .	NHEt		
CH=CHCH2CH3	Me	4-morpholinyl		
CH=CHCH2CF3	Hex	pyrrolidinyl		
CH=CC1	Et.	piperidinyl		

Ph	OBu	C1 .
PhO	OCH <sub>2</sub> CF <sub>3</sub>	Br
4-Me-Ph	O(CH <sub>2</sub> ) <sub>3</sub> CF <sub>3</sub>	F .
3-CF <sub>3</sub> -Ph	CH <sub>2</sub> OMe	CIN
4-i-Pr-PhO	(CH <sub>2</sub> ) 30Me	ОН
4-F <sub>2</sub> HCO-Ph	СН=СНМе	Me
3-Et-PhO	сн=снсн <sub>2</sub> сн <sub>3</sub>	Hex
4-MeO-PhO	CH=CHCH2CF3	Et
4-MeO-Ph	CH=CC1 <sub>2</sub>	i-Pr
·	OCH2CH=CH2	c-Pr
G <sup>2</sup> =S, Y=N, X=CH,	CH2CH2OMe	c-Hex
R <sup>10</sup> =H	OCHF <sub>2</sub>	2-Me-c-Pr
R <sup>9</sup>	C≡CH	CF3
H	C=CCH <sub>2</sub> CH <sub>3</sub>	(CH <sub>2</sub> ) 3CF3
Cl	OCH <sub>2</sub> C≡CH	SMe
Br .	NH <sub>2</sub>	SBu
F	NMe <sub>2</sub>	5 (O) Me
CN	NHEt	S (0) Bu
OH.	4-morpholinyl	S (0) <sub>2</sub> Me
Me .	pyrrolidinyl	S (0) 2Bu
Hex	piperidinyl	OMe
Et	Ph	OBu
i-Pr	PhO	OCH <sub>2</sub> CF <sub>3</sub>
c-Pr	4-Me-Ph	O(CH <sub>2</sub> )3CF3
c-Hex	3-CF <sub>3</sub> -Ph	CH <sub>2</sub> OMe
2-Me- <i>c</i> -Pr	4-i-Pr-PhO	(CH <sub>2.</sub> ) 30Me
CF <sub>3</sub>	4-F <sub>2</sub> HCO-Ph	Сн=Снме
(CH <sub>2</sub> ) <sub>3</sub> CF <sub>3</sub>	3-Et-PhO	сн=снсн <sub>2</sub> сн <sub>3</sub>
SMe	4-MeO-PhO	CH=CHCH2CF3
SBu	4-MeO-Ph	CH=CCl <sub>2</sub>
S (0) Me		OCH2CH=CH2
S (O) Bu	$G^2=S$ , $R^9=R^{10}=Me$ ,	CH <sub>2</sub> CH <sub>2</sub> OMe
S (O) 2Me	X=CR <sup>13</sup> , Y=N	OCHF <sub>2</sub>
S (O) 2Bu	R <sup>13</sup>	C≡CH
OMe	н	C≡CCH <sub>2</sub> CH <sub>3</sub>

a i	1	
och <sub>2</sub> c≡ch	F	NMe <sub>2</sub>
NH <sub>2</sub> . :	CN	NHEt
NMe <sub>2</sub>	OH	4-morpholinyl
NHEt	Me	pyrrolidinyl
4-morpholinyl	Hex	piperidinyl
pyrrolidinyl .	Et	Ph
piperidinyl	í-Pr	PhO
Ph	c-Pr	4-Me-Ph
PhO	c-Hex	3-CF <sub>3</sub> -Ph
4-Me-Ph	2-Me-c-Pr	4-i-Pr-PhO
3-CF <sub>3</sub> -Ph	CF <sub>3</sub>	4-F <sub>2</sub> HCO-Ph
4-i-Pr-PhO	(CH <sub>2</sub> ) <sub>3</sub> CF <sub>3</sub>	3-Et-PhO
4-F <sub>2</sub> HCO-Ph	SMe	4-MeO-PhO
3-Et-PhO	SBu	4-MeO-Ph
4-MeO-PhO	5 (O) Me	•
4-MeO-Ph	S (0) Bu	$G^{2}=0$ , $R^{9}=R^{10}=Me$ ,
	S (O) 2Me	X=CR <sup>13</sup> , Y=N
G <sup>2</sup> =S, R <sup>9</sup> =R <sup>10</sup> =Me,	S (O) 2Bu	R <sup>13</sup>
X=CH, Y=CR <sup>14</sup>	OMe	H
R <sup>14</sup>	OBu	CI
Cl	OCH2CF3	Br
Br	0 (CH <sub>2</sub> ) 3CF3	F
F .	CH <sub>2</sub> OMe	CIN .
Me	(CH <sub>2</sub> ) 30Me	OH .
Et	СН=СНМе	Me
OMe	CH=CHCH <sub>2</sub> CH <sub>3</sub>	Hex
OEt	CH=CHCH <sub>2</sub> CF <sub>3</sub>	Et.
H	CH=CC1 <sub>2</sub>	f-Pr .
	OCH2CH=CH2	c-Pr
$G^2=0$ , Y=N, X=CH,	CH <sub>2</sub> CH <sub>2</sub> OMe	· c-Hex
R10=H	OCHF <sub>2</sub>	2-Me-c-Pr
R <sup>g</sup>	C≡CH.	CF3
H	C=CCH2CH3	(CH <sub>2</sub> ) <sub>3</sub> CF <sub>3</sub>
CI	OCH <sub>2</sub> C≡CH	SMe
Br	NH <sub>2</sub>	SBu

	1	
S (O) Me		Ph
S (0) Bu	$G^2=0$ , $R^9=R^{10}=Me$ ,	PhO
S (0) 2 <sup>Me</sup>	X=CH, Y=CR <sup>14</sup>	4-Me-Ph
S (0) 2Bu	B <sup>14</sup>	4-MeO-Ph
OMe	CI ,	H
ОВи	Br	,
OCH <sub>2</sub> CF <sub>3</sub>	F	$G^2=S$ , $R^9=Me$ , Y=CH,
O(CH <sub>2</sub> ) <sub>3</sub> CF <sub>3</sub>	Ме	X=N
CH <sub>2</sub> OMe	Et ·	R <sup>10</sup>
(CH <sub>2</sub> ) <sub>3</sub> OMe	OMe	CI
СН=СНМе	OEt	Br
CH=CHCH2CH3	<b>H</b> (	F
CH=CHCH2CF3		CIN
CH=CCl <sub>2</sub>	G <sup>2</sup> =S, R <sup>9</sup> =Me, X=Y=N	ОН
OCH <sub>2</sub> CH=CH <sub>2</sub>	R <sup>10</sup> .	Me
CH <sub>2</sub> CH <sub>2</sub> OMe	Cl	Et
OCHF <sub>2</sub>	Br	i-Pr
C=CH	F .	c-Pr
C≡CCH2CH3	CN	CF <sub>3</sub>
OCH <sub>2</sub> C≡CH	ОН	SMe
NH <sub>2</sub>	Me	S (0) Me
NMe <sub>2</sub>	Et	S (0) 2 <sup>Me</sup>
NHEt	i-Pr	OMe
4-morpholinyl	c-Pr	OEt
pyrrolidinyl	CF <sub>3</sub>	OCH <sub>2</sub> OMe
piperidinyl	SMe .	OCH <sub>2</sub> CF <sub>3</sub>
Ph	S (0) Me	C=CHMe
PhO	S (O) 2Me	C≡CMe
4-Me-Ph	OMe .	NMe <sub>2</sub>
3-CF <sub>3</sub> -Ph	OEt	Ph
4-i-Pr-PhO	OCH <sub>2</sub> OMe	PhO
4-F2HCO-Ph	OCH <sub>2</sub> CF <sub>3</sub>	4-Me-Ph
3-Et-PhO	C=CHMe	4-MeO-Ph .
4-MeO-PhO	C≡CMe	н
4-MeO-Ph	NMe <sub>2</sub>	

G <sup>2</sup> =0, R <sup>9</sup> =Me	, X=Y=N	С=СНМе	-	i-Pr	•
R <sup>10</sup>	·	C≡CMe		c-Pr	
CJ		NMe <sub>2</sub>		CF3	
Br		Ph		SMe	
F	1	Pho		S (0) Me	
CIN		4-Me-Ph		S (0) 2Me	:-
OH		4-MeO-Ph		· OMe	•
Me		н .		OEt	
Et		•		OCH <sub>2</sub> OMe	
i-Pr		G <sup>2</sup> =0, R <sup>9</sup> =Me	, Y=CH,	OCH <sub>2</sub> CF <sub>3</sub>	
c-Pr	. ,	X=N		C=CHMe	
CF <sub>3</sub>		R <sup>10</sup>		C≡CMe	
SMe	1.	Cī		NMe <sub>2</sub>	
S (0)Me		Br	•	Ph ·	
S(0) <sub>2</sub> Me		F		PhO	
OMe ·	1	CIÀ	-	4-Me-Ph	
OEt		OH ·		4-MeO-Ph	
OCH <sub>2</sub> OMe		Me		H.	٠.
OCH <sub>2</sub> CF <sub>3</sub>	1	Et .		× .	
			1		•
G <sup>2</sup> =S			:	•	
X	Ÿ	R14	R <sup>9</sup> .	R <sup>13</sup>	R <sup>10</sup>
N :	CR14	-(CH <sub>2</sub> ) <sub>3</sub> -	:		Me
CH	CR14	-(CH <sub>2</sub> ) <sub>3</sub> -			Me
N	CR14	-(CH <sub>2</sub> ) <sub>4</sub> -		<del></del> -	Me
CH	CR14	-(CH <sub>2</sub> ) <sub>4</sub> -		<u> </u>	Me
CR13 ·	N		-(CH <sub>2</sub> ) <sub>3</sub> -		Me
CR <sup>13</sup>	CH .		-(CH <sub>2</sub> ) <sub>3</sub> -		Me
CR13	N	, <del></del>	-(CH <sub>2</sub> ) <sub>4</sub> -		Me
CR13	CH .	<b></b> .	-(CH <sub>2</sub> ) <sub>4</sub> -		Me
CR <sup>13</sup>	CH		Me	- (CH <sub>2</sub> ) <sub>3</sub> -	•
CR13.	CH .	•	Ме	-(CH <sub>2</sub> ) <sub>4</sub> -	

G <sup>2</sup> =O	•				
x	¥	B <sup>14</sup> .	R <sup>9</sup>	B13	B10
N	CR <sup>14</sup>	-(CH <sub>2</sub> )	<b>3</b>	, <del></del>	Me
СН	CR14	-(CH <sub>2</sub> )		. <del></del>	Ме
N	CR14	-(CH <sub>2</sub> )	4-		Me
СН	CR14	-(CH <sub>2</sub> )	4-		Me
CR13	N		-(CH <sub>2</sub> ) <sub>3</sub>	-	Me
CR13	CH		-(CH <sub>2</sub> ) <sub>3</sub>		Me
CR13	N.		- (CH <sub>2</sub> ') 4		Me
CR13	СН		- (CH <sub>2</sub> ) 4	-	Me
CR13	CH		Me	- (CH <sub>2</sub>	,) <sub>3</sub> -
CR13	CH -	<del></del>	Me	- (CH <sub>2</sub>	

## Compounds of Formula Ie

R10	1	
K-0	c-Pr	C=CHMe
CJ	CF <sub>3</sub>	C≡CMe
Br	SMe	NMe <sub>2</sub>
<b>F</b>	S (O) Me	Ph
CN	S (0) 2Me	PhO
ОН	OMe	4-Me-Ph
Ме	OEt.	4-MeO-Ph
Et	OCH <sub>2</sub> OMe	н
i-Pr	OCH <sub>2</sub> CF <sub>3</sub>	

G <sup>2</sup> =S		•			•	
x	· <b>x</b>	R10	R <sup>11</sup>	R <sup>12</sup>	R <sup>28</sup>	R31
CH	N.	Me	. Н	н	H	H
и .	СН	. Me	H	н	H	H
N	N	Me	Н	3-Me	4-Me	H
N	N	Me	H	3-Me	4-Me	6-Me
N	N	Me	Me	н	н	7-Me

Δ	1
-	

N.	и.	Me	H.	н	4-1-Pr	6-OMe
N	N	Ме	H	3-Me	H	7-CF3
N	N	Ме	H	H	4-Et	7-Et
N	N	Me.	Ħ	H .	4-1-Pr	6-OCHF <sub>2</sub>
N	N	Me	H	н	H	8-Bu
N	и .	. Me	H	н	4-c-Pr	6-OEt

$G^2=0$ , X=Y=N, $R^{11}=R^{12}$	-R <sup>28</sup> -H	
R <sup>10</sup>	c-Pr	C=CHMe
cı ·	CF3	C≡CMe
Br	SMe	NMe <sub>2</sub>
F	S (0) Me .	Ph
CN	S (0) 2Me	PhO
ОН	OMe	4-Me-Ph
Me	OEt	4-MeO-Ph
Et	OCH <sub>2</sub> OMe	H.
1-Pr	OCH2CF3	

G~=O				•••		
x	¥	R <sup>10</sup>	R <sup>11</sup>	R <sup>12</sup>	R <sup>28</sup>	R <sup>31</sup>
CH	N	Me .	н .	H	<b>H</b>	H
N	CH .	Me	H	H	H .	E
N	, N	Me	H	3-Me	4-Me	H
N	N	Me .	H	3-Me	4-Me	6-Me
N .	Ň	Me	Me '	<b>H</b> 1.1.	н	7-Me
N	N	Me	<b>H</b>	H	4-1-Pr	6-OMe
N	N	Me	H	3-Me	H	7-CF3
N	N	Me	H	H	4-Et	7-Et
N	N	Me	Ħ	H	4- <i>i</i> -Pr	6-ochf <sub>2</sub>
и.	N	Me	Ħ	н	H	8-Bu
и .	N	Me	H	Ħ	4-c-Pr	6-OEt

Comboun	os or	Formuta	TE
2	4 4	10	

	compounds of solutions ar			
$G^{2}=S$ , $R^{12}=H$ , $R^{28}=H$	G <sup>2</sup> =S, R <sup>11</sup> =R <sup>12</sup> =H	4-0=0	H	
R <sup>11</sup>	R <sup>28</sup>	4-C=C	:-Et	
н .	4-Me	4-0CF	I <sub>2</sub> C≡CH	
Me ·	4-CN	4-NMe	2	
Et	4-NO <sub>2</sub>	i	O) NMe <sub>2</sub>	
i-Pr	4-OH	4-Ph		
<i>s</i> -Bu	4-CO <sub>2</sub> H	4-0Ph		
. · <b>F</b> * :	4-co <sub>2</sub> Et	4-SPb	ı	
cı .	4-Et	4-(3-	Me-Ph)	
Br	4-i-Pr		i	
CF <sub>3</sub>	4-n-Hex	Ģ <sup>2</sup> −S		
OMe	4-c-Pr	B <sup>11</sup>	R <sup>12</sup>	R <sup>28</sup>
OEt	4-CF3	Cl	н	6-C1
OCHF <sub>2</sub>	4-SMe	н	3-Me	4-Me
OBu	4-SBu	н	3-Me	4-Et
O(CH <sub>2</sub> ) <sub>3</sub> CF <sub>3</sub>	4-c-Hex	н	3-ОМе	4-OMe
(CH <sub>2</sub> ) <sub>3</sub> CF <sub>3</sub>	4-C1	Me	H .	5-Me
$G^2=S$ , $R^{11}=H$ , $R^{28}=H$	4-Br .	Me	H	4-Me
R <sup>12</sup>	4-F .	Me	4-Me	5-Me
3-Me	4-(CH <sub>2</sub> ) <sub>3</sub> CF <sub>3</sub>	H	3-C1	5-C1
3-Et	4-S (0) Me	Cl	·H	4-Cl
3-1-Pr	4-S (O) Bu			
3- <i>9</i> -Bu	4-S (O) 2Me	. G <sup>2</sup> =0,	R <sup>12</sup> =H,	R <sup>28</sup> ≂H
3-F	4-S (O) 2Bu	R <sup>11</sup>		
3-Cj	4-OMe	H		
3-Br	4-OBu	Me	"···	
3-CF <sub>3</sub>	4-OCH <sub>2</sub> CF <sub>3</sub>	Et		
3-OMe	4-OCH <sub>2</sub> OMe	'i-Pr		
3-oet	4-CH <sub>2</sub> OMe	s-Bu		•
3-OCHF <sub>2</sub>	4-CH=CH-Me	F		
3-0Bu :	4-CH=CHCH2Me	Cl		
3-0 (CH <sub>2</sub> ) <sub>3</sub> CF <sub>3</sub>	4-TBS	Br		
3-(CH <sub>2</sub> ) <sub>3</sub> CF <sub>3</sub>	4-SiMe <sub>3</sub>	CF <sub>2</sub>		

· ·				
OMe .	4-c-Pr	н 3-ме 4-ме		
OEt	4-CF3	H 3-Me 4-Et		
OCHF <sub>2</sub>	4-SMe	H 3-OMe 4-OMe		
OBu	4-SBu	ме н 5-ме		
O(CH <sub>2</sub> ) <sub>3</sub> CF <sub>3</sub>	4-c-Hex	Me H 4-Me		
(CH <sub>2</sub> ) <sub>3</sub> CF <sub>3</sub>	4-C1	Me 4-Me 5-Me		
	4-Br	H 3-C1 5-C1		
G <sup>2</sup> =0, R <sup>11</sup> =H, R <sup>28</sup> =H	4-F	CL H 4-Cl		
R <sup>12</sup>	4-(CH <sub>2</sub> ) <sub>3</sub> CF <sub>3</sub>			
3-Me	4-S (0) Me	$G^2=S(0), R^{12}=H,$		
3-Et	4-S (O) Bu	$R^{28}=H$		
3-1-Pr	4-S (0) 2Me	R <sup>11</sup>		
3- <i>s</i> -Bu	4-S (O) 2Bu	<b>H</b>		
3-F	4-OMe	Me		
3-CI	4-0Bu	Et		
3-Br	4-OCH <sub>2</sub> CF <sub>3</sub>	i-Pr		
3-CF <sub>3</sub>	4-OCH <sub>2</sub> OMe	s-Bu		
3-ОМе	4-CH <sub>2</sub> OMe	F		
3-0Et	4-CH=CH-Me	Cl		
3-OCHF <sub>2</sub>	4-CH=CHCH <sub>2</sub> Me	Br.		
3-0Bu	4-TBS	CF <sub>3</sub>		
3-0 (CH <sub>2</sub> ) 3CF <sub>3</sub>	4-SiMe3	OMe .		
3-(CH <sub>2</sub> ) <sub>3</sub> CF <sub>3</sub>	4-C≡CH	OEt		
	4-C≡C-Et	OCHF <sub>2</sub>		
G <sup>2</sup> =0, R <sup>11</sup> =R <sup>12</sup> =H	4-0CH <sub>2</sub> C=CH	OBu		
R <sup>28</sup>	4-NMe <sub>2</sub>	O (CH <sub>2</sub> ) 3CF3		
4-Me	4-C(=0) NMe <sub>2</sub>	(CH <sub>2</sub> ) <sub>3</sub> CF <sub>3</sub>		
4-CN	4-Ph			
4-NO <sub>2</sub>	4-0Ph	$G^2=S(0)$ , $R^{11}=H$ ,		
4-OH	4-SPh	R <sup>28</sup> =H		
4-co <sub>2</sub> H	4-(3-Me-Ph)	<b>E</b> <sup>12</sup>		
4-C0 <sub>2</sub> Et		3-Me		
4-Et	G <sup>2</sup> =0	3-Et		
4-i-Pr	R <sup>11</sup> R <sup>12</sup> R <sup>28</sup>	3-1-Pr		
4-n-Hex	CT H 6-CT	3- <i>s</i> -Bu		
	•			

3.5	4-0Me		1	Me
3-F		*		Et
3-C1	4-0Bt			i-Pr
3-Br	•	I <sub>2</sub> CF <sub>3</sub>		
3-CF <sub>3</sub>		1 <sub>2</sub> OMe		s-Bu
3-OMe	4-CH <sub>2</sub>			F .
3-OEt		=CH-Me		Cl
3-OCHF <sub>2</sub>		=CHCH <sub>2</sub> Me		Br
3-OBu	4-TBS			CF <sub>3</sub>
3-0 (CH <sub>2</sub> ) <sub>3</sub> CF <sub>3</sub>	4-Sin	le <sub>3</sub>		OMe
3-(CH <sub>2</sub> ) <sub>3</sub> CF <sub>3</sub>	4-C=C	CH		OEt
	4-C≡(	:-Et		OCHF <sub>2</sub>
$G^2=S(0), R^{11}=R^{12}=H$		H <sub>2</sub> C≡CH	•	OBu
R <sup>28</sup> ·	4-NM	€2		O(CH <sub>2</sub> ) <sub>3</sub> CF <sub>3</sub>
4-Me .	4-C (=	=0) NMe <sub>2</sub>		(CH <sub>2</sub> ) <sub>3</sub> CF <sub>3</sub>
4-CN	4-Ph			
4-NO <sub>2</sub>	4-OP1	h.	·	$G^{2}=S(0)_{2}, R^{11}=H,$
4-OH	4-SPI	h		R <sup>28</sup> ≖H
4-co <sub>2</sub> H	4-(3-	-Me-Ph)	•	R <sup>12</sup>
4-co <sub>2</sub> Et				3-Me
4-Et	G <sup>2</sup> =S	(0)		3-Et
4- <i>i</i> -Pr	<b>R</b> 11	R <sup>12</sup>	R <sup>28</sup>	3- <b>1-</b> Pr
4-n-Hex	Cl	H	6-C1	3- <i>s</i> -Bu
4-c-Pr	H	3-Me	4-Me	3-F
4-CF <sub>3</sub>	· <b>H</b>	3-Me	4-Et	3-C1
4-SMe	H	3-ОМе	4-OMe	3-Br
4-SBu	Me	H	5-Me	3-CF3
4- <i>c</i> -Hex	Me	н	4-Me	3-0Me
4-C1	Me	4-Me	5-Me	3-OEt
4-Br	H	3-C1	5-C1	3-OCHF2
4-F	CI	H	4-Cl	3-OBu
4-'(CH <sub>2</sub> ) 3CF3	•			3-0 (CH <sub>2</sub> ) 3CF <sub>3</sub>
4-S·(0) Me	G <sup>2</sup> =S	(0) <sub>2</sub> , R <sup>1</sup>	.2 <sub>=H</sub> ,	3-(CH <sub>2)3</sub> CF3
4-S (O) Bu	R <sup>28</sup> =	н	•	
4-S (O) 2Me	R11		61	
4-S (O) 2Bu	н			

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G^2=S(0)_2,
R^{11}=R^{12}=H
Ř<sup>28</sup>
4-Me
4-CN
4-NO2
4-0H
4-co2H
4-CO<sub>2</sub>Et
4-Et
4-1-Pr
4-n-Hex
4-c-Pr .
4-CF'3
4-SMe
4-SBu
4-c-Hex
4-C1
4-Br
4-F
4-(CH<sub>2</sub>)<sub>3</sub>CF<sub>3</sub>
4-S (O) Me
4-S (O) Bu
4-S (O) 2Me
4-S (0) 2Bu
4-0Me
4-OBu
4-OCH<sub>2</sub>CF<sub>3</sub>
4-0CH20Me
 4-CH<sub>2</sub>OMe
```

4-сн-сн-ме 4-CH=CHCH<sub>2</sub>Me 4-TBS 4-SiMe3 4-C=CH 4-C≡C-Et 4-OCH2C≡CH 4-NMe2 -4-C (=0) NMe2 4-Ph 4-OPh 4-SPh 4-(3-Me-Ph)  $G^2=S(0)_2$  $R^{11}$ B12 R<sup>28</sup> CI H 6-Cl H 3-Me 4-Me Ħ 3-Me 4-Et 3-оме 4-OMe H Ħ Me 5-Me H 4-Me Me 4-Me 5-Me Me H 3-C1 5-C1 ·CI H 4-C1

H

#### TABLE 4

Compounds	of	Formula	Ig
		Et	

 $n^{1}=1$ R<sup>27</sup> Bu H i-Pr CHF<sub>2</sub> Et Bu  $(CH_2)_3CF_3$ CO<sub>2</sub>Et i-Pr CHF<sub>2</sub> C (=0) Me (CH<sub>2</sub>) 3CF3 C (=0) (CH2) 3Me CO<sub>2</sub>Et C (=0) Ph C (=0) Me (3-Me-Ph) C (=O). C (=0) (CH<sub>2</sub>) 3Me (4-OMe-Ph)C(=O) C (=0) Ph CH2C=CH2 сн2с≡сн (3-Me-Ph)C(=0) PhCH<sub>2</sub> (4-OMe-Ph) C (=O) CH2C=CH2 4-Me-PhCH<sub>2</sub> CH<sub>2</sub>C≡CH S (0) <sub>2</sub>Me  $PhCH_2$ C (=0) NMe2 4-Me-PhCH<sub>2</sub> C (=S) NHMe S (0) Me S (=0) 2Me S (0) 2Ph C (=0) NMe2 C (=S) NHMe (4-Me-Ph) S (0) 2 S (0) Me C (=0) NHPh C (=S) NHPh S (0) 2Ph P (=S) (OEt) 2 (4-Me-Ph)S(0)2 P (=0) (OEt) 2 C (=0) NHPh C (=S) NHPh S(0)2N(Et)2 P (=S) (OEt) 2 n<sup>1</sup>=3 P (=0) (OEt) 2 R27 5 (0) 2N (Et) 2 n<sup>1</sup>=2 H Et B<sup>27</sup> Bu

i-Pr

	•							•
		•	5	0				
	CHF <sub>2</sub>			1	. 1		S (O)	
	(CH <sub>2</sub> ) <sub>3</sub> CF <sub>3</sub>	,		1	. 2		s (o)	
	CO2Et	,		2	1		S (O)	
	C (=0) Me	•		σ	3		S (O)	
	C (=0) (CH <sub>2</sub>	o) aMe		1	1	•	S(0)2	
	C(=0)Ph			. 1	· 2		S(0)2	
	(3-Me-Ph)	C (=0)		. 2	1		S (0) 2	
	(4-OMe-Ph	. :		a	· 3	•	S (0) 2	-
	CH2C=CH2		•	· · 1	. 1	٠.	N-Me	
	сн <sub>2</sub> с≡сн	•	٠.	1	. 2		N-Me	
	PhCH <sub>2</sub>			2	1		N-Me	•
	4-Me-PhCE	12			•			
	S (0) 2Me	•			TAI	LE 6		
	C (=0) NMe2	2		d	compounds of	For	mula I	Ŀ
	C (=S) NHMe			· G <sup>2</sup> =\$	•			
	S (O) Me			n <sup>2</sup>	<b>R</b> <sup>1</sup> .	<b>B</b> 7	R4	R8
	S (0) 2Ph	•		. 1	Me	H.	H	Ħ
	(4-Me-Ph)	S(0)2		1	Bu .	Ħ	H	H.
	C (=0) NHP1	1	•	1	Me	Me	Ħ	H
	C (=S) NHP1		•	1	H	H	Me '	Ħ
	P (=S) (OEt	=)2		1	Ħ.	H	Bu	H
	P (=0) (OEt	12		1	Ph	H	Ħ	H
	S (0) 2N (Et	=) <sub>2</sub> "		1	4-Me-Ph	H	H	H
			•	1	4-OMe-Ph	н.	H	H.
	•	TABLE 5		Ó	Me	H		
	Сотро	ounds of For	•	0	Bu	, <b>H</b>		
	n -	n <sup>1</sup>	$\mathbf{G}^2$	0	Me	Me		
	1	1	s .	0	Ph	H		
	1	2	s ·	0	4-Me-Ph	H		
	2	1	s					
٠	0 [	3	S	G <sup>2</sup> =0		_		
	1	1	0	n <sup>2</sup>	R <sup>1</sup>	R7	<u>R</u> 4	<b>B</b> 8
	: 1	2 · ·	0	1	Me	H	H	H
	2	1	0	1	Bu	. <b>H</b>	H	H
		_					٠	••

51.

1	H	н	Me	H		1	4-Me-Ph	Н	н
1	н	н	Bu	н		1	H	Ph	H
1	Ph	н	н	H		1	H	4-Me-Ph	н
1	4-Me-Ph	H	н	H		1	Н	H	Ph
1	4-OMe-P	h, H	н	H		1	H	н	4-Me-Ph
0	. Me	H							
0	Bu	H	,			G <sup>2</sup> -	<b>=</b> 0		
O,	Me	Me				n <sup>2</sup>	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>
0	Ph	. н				0	Me ·	н	
0	4-Me-Ph	н				0	Bu	H	·
						0	н -	Me .	
	2	TABLE	Z.			0	H	Bu	
	Compounds	of Fo	cmula	Ij		0	Ph :	H	
G <sup>2</sup>	=S			•		0	4-Me-Ph	H	
n <sup>2</sup>	R <sup>1</sup>	R <sup>2</sup>		R <sup>3</sup>		0	<b>H</b> ,/	4-OMe-Ph	
0	Me	H			.	1	Me .	H	H
0	Bu	H				1	Bu	Н	H
0	H	Me				$n^2$	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>
0	H	Bu				1	н	Me .	H
0	Ph	H				1	н	. Bu	Н
0 -	4-Me-Ph	H				1	H	H	Me
0	н	4-OMe	-Ph		ŀ	1	н	H ,	Bu
1	Me	H		Н		1	Ph	H	H
1	Bu	H	-7	H		n <sup>2</sup>	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>
1	H	Me .		H		1	4-Me-Ph	Н	н .
. 1	H	Bu		H	.	1	H	Ph	Н
1	H	H .	-	Me		1	H	4-Me-Ph	H
1	Н .	H		Bu		1	H	Н	Ph
1	Ph	H		H	1	1	H	н	4-Me-Ph

# Compounds of Formula Ik

$G^2=S$				н	- <b>H</b>	Ph	H	
R1	<b>B</b> <sup>7</sup>	<b>R</b> <sup>5</sup>		н	н	н	Me	
н	• н	Me	н	H	н	н	- Ph	

_	2
	_

								•
	Ме	H	H Comment	н .	Ph	H	H	. <b>H</b>
	Ме	Me	H	н .	н	Ph	H	H
	Ph	H	H	H.,	H .	H	Bu	H
	H .	Ph	H.	R	H	Ħ.	4-Me-Ph	H
	H	H	Bu	H	H	H .	H	Bu
	H	н	4-Me-Ph	H	H	H	Ħ	4-OMe-Ph
	н .	H.	H	Bu	Bu	H	H	H
	H	H	H	4-OMe-Ph	3-Me-Ph	н .	H .	Ħ.
	Bu	H	H	H	4-OMe-Ph	H	н .	H
	3-Me-Ph	н.	Ħ .	H				
	4-OMe-Ph	Ħ	H ·	H		-	•	
	G <sup>2</sup> ≕O	•	-					
	R <sup>1</sup>	R7	B <sup>5</sup>	R <sup>6</sup>	,			
	H .	H	Me	н			•	٠.
	H	н	Ph	н			٠.	
	Ħ	H	H	Me.			• •	
	H	H	н	Ph				
	Mer	H	<b>H</b> .	н }			_	•
•	Me	Me	<b>H</b> .	н			•	

#### Compounds of Formula II

·	Compounds of	Formula II
G <sup>2</sup> =S		3-thienyl
<u>E</u>	•	2,5-diMe-3-furanyl
H		2,5-diMe-3-thienyl
Me		4-Me-PhO
n-Hex		2-C1-PhO
c-Hex		2,6-diMe-PhO
PhCH <sub>2</sub>		4-Me-PhŅH
CH2CH2CF3		3-Me-PhS
OBů	• •	s-BuS
0(CH <sub>2</sub> )5C1		1-indanyl
1-naphthalenyl		5-Me-2-thienyl
2-naphthalenyl		5-Me-2-pyridyl
2-furanyl	: (	4-Me-3-furanyl

```
2-Me-3-pyridyl
                                         c-Hex
                                         PhCH<sub>2</sub>
G<sup>2</sup>=0
                                         CH2CH2CF3
E
                                         OBu
H
                                         O(CH2)5C1
Me
                                         1-naphthalenyl
n-Hex
                                         2-naphthalenyl
c-Hex
                                         2-furanyl
PhCH<sub>2</sub>
                                         3-thienyl
CH2CH2CF3
                                         2,5-diMe-3-furanyl
OBu
                                         2,5-diMe-3-thienyl
O(CH<sub>2</sub>)5C1
                                         4-Me-PhO
1-naphthalenyl
                                         2-C1-PhO
2-naphthalenyl
                                         2,6-diMe-PhO
2-furanyl
                                         4-Me-PhNH
3-thienyl
                                         3-Me-PhS
2,5-diMe-3-furanyl
                                         s-BuS
2,5-diMe-3-thienyl
                                         1-indanyl
4-Me-PhO
                                         5-Me-2-thienyl
2-C1-Ph0
                                         5-Me-2-pyridyl
2,6-diMe-PhO
                                         4-Me-3-furanyl
4-Me-PhNH
                                         2-Me-3-pyridyl
3-Me-PhS
                                         G2=S (0)2
s-BuS
1-indanyl
                                         E
5-Me-2-thienyl
5-Me-2-pyridyl
                                         Me
4-Me-3-furanyl
                                         n-Hex
2-Me-3-pyridyl
                                         c-Hex
                                         PhCH<sub>2</sub>
G2≔S (O)
                                         CH2CH2CF3
                                         OBu
H
                                         0 (CH<sub>2</sub>) 5C1
                                         1-naphthalenyl
Me
n−Hex
                                         2-naphthalenyl
```

54

2-furanyl 3-Me-PhS
3-thienyl s-BuS
2,5-diMe-3-furanyl 1-indanyl
2,5-diMe-3-thienyl 5-Me-2-thienyl
4-Me-PhO 5-Me-2-pyridyl
2-Cl-PhO 4-Me-3-furanyl
2,6-diMe-PhO 2-Me-3-pyridyl
4-Me-PhNH

## TABLE 10

	•	•	Compounds of	Formula:	IIIc	
$\mathbf{G}^{2}$	n	$n^{1}$		s (O)	1	1
s .	0	ı '		S (O)	1	. 2
S	σ	2.		s (O)	2	1
S	0	3	- A Y	s (0) 2	0	1
S	1.	1		s(0)2	Ο.	` 2
S	1	2		s(0) <sub>2</sub>	0	3.
s	. 2	1 .		S(0)2	1	1
0	,O	1		S(0)2	1	2
0	Ð	2	·	S (0) 2	2	1
·	0	3		. NMe.	0 .	. 1
0	1	1	•	NMe .	-0-	. 2
0	1	2	•	NMe	0	3
0	2	1.		NMe	1	1
S (O)	o.	1		NMe	1	2
S (O)	0	2		NMe	2	1
S (O)	O	3				

	Compounds of Form	nula IIc
G <sup>2</sup> -S, R <sup>9</sup> -Me, Y=N,	Br	Hex
X=CH	F	Et
R <sup>10</sup>	CIA	i-Pr
<b>H</b>	ОН	C-PI
CI	Me	c-Hex

	1	
2-Me-c-Pr	4-i-Pr-PhO	(CH <sub>2</sub> ) <sub>3</sub> OMe
CF <sub>3</sub>	4-F2HCO-Ph	СН=СНМе
(CH <sub>2</sub> ) <sub>3</sub> CF <sub>3</sub>	3-Et-PhO	сн=снсн <sub>2</sub> сн <sub>3</sub>
SMe	4-MeO-PhO	CH=CHCH <sub>2</sub> CF <sub>3</sub>
SBu	4-MeO-Ph	CH=CC12
S (O) Me		OCH2CH=CH2
S (O) Bu	$G^2=0$ , $R^9=Me$ , Y=N,	CH <sub>2</sub> CH <sub>2</sub> OMe
S (0) <sub>2</sub> Me	X=CH	OCHF <sub>2</sub>
S (O) <sub>2</sub> Bu	R <sup>10</sup>	C=CH
OMe William	<b>н</b>	C≡CCH <sub>2</sub> CH <sub>3</sub>
OBu	Cl	och <sub>2</sub> c≡ch
OCH <sub>2</sub> CF <sub>3</sub>	Br	NH <sub>2</sub>
O(CH <sub>2</sub> ) <sub>3</sub> CF <sub>3</sub>	F.	NMe <sub>2</sub>
CH <sub>2</sub> OMe	CN	NHEt
(CH <sub>2</sub> ) <sub>3</sub> OMe	ОН	4-morpholinyl
СН=СНМе	Me	pyrrolidinyl
CH=CHCH <sub>2</sub> CH <sub>3</sub>	Hex	piperidinyl
CH=CHCH <sub>2</sub> CF <sub>3</sub>	Et	Ph
CH=CCl <sub>2</sub>	i-Pr	PhO
OCH <sub>2</sub> CH=CH <sub>2</sub>	c-Pr	4-Me-Ph
CH <sub>2</sub> CH <sub>2</sub> OMe	с-Нех	3-CF <sub>3</sub> -Ph
OCHF <sub>2</sub>	2-Me-c-Pr	4-i-Pr-PhO
C≡CH	CF <sub>3</sub>	4-F <sub>2</sub> HCO-Ph
C≡CCH <sub>2</sub> CH <sub>3</sub>	(CH <sub>2</sub> ) <sub>3</sub> CF <sub>3</sub>	3-Et-PhO
OCH <sub>2</sub> C≡CH	SMe ·	4-MeO-PhO °
NH <sub>2</sub>	SBu	4-MeO-Ph
NMe <sub>2</sub>	S(0)Me .	
NHEt	S (0) Bu	$G^2=S$ , Y=N, X=CH,
4-morpholinyl	S (0) 2Me	$R^{10}=H$
pyrrolidinyl	S (0) 2Bu	R <sup>9</sup>
piperidinyl.	OMe .	<b>H</b>
Ph .	OBu	<b>C1</b>
PhO	OCH <sub>2</sub> CF <sub>3</sub>	Br
4-Me-Ph	O(CH <sub>2</sub> ) <sub>3</sub> CF <sub>3</sub>	F
3-CF <sub>3</sub> -Ph	CH <sub>2</sub> OMe	CN

OH I	4-morpholiny1
:	pyrrolidinyl
Me	
Hex	piperidinyl
Et	Ph
i-Pr	PhO
c-Pr	4-Me-Ph
c-Hex	3-CF <sub>3</sub> -Ph
2-Me-c-Pr	4-i-Pr-PhO
CF <sub>3</sub>	4-F <sub>2</sub> HCO-Ph
(CH <sub>2</sub> ) 3CF <sub>3</sub>	3-Et-PhO
SMe	4-MeO-PhO
SBu -	4-MeO-Ph
S (0) Me	
S (0) Bu	$G^2=S$ , $R^9=R^{10}=Me$ ,
S (0) 2Me	X=CR <sup>13</sup> , Y=N
S (0) 2Bu	R <sup>13</sup>
OMe	н
OBu	CI CI
OCH <sub>2</sub> CF <sub>3</sub>	Br
O(CH <sub>2</sub> ) <sub>3</sub> CF <sub>3</sub>	· F
CH <sub>2</sub> OMe	CN
(CH <sub>2</sub> ) <sub>3</sub> OMe	OH
CH=CHMe -	Me
CH=CHCH2CH3	Hex
CH=CHCH <sub>2</sub> CF <sub>3</sub>	Et
CH=CCI <sub>2</sub>	i-Pr
OCH2CH=CH2	c-Pr
CH <sub>2</sub> CH <sub>2</sub> OMe	c-Hex
OCHF <sub>2</sub>	2-Me-c-Pr
C=CH	CE3
C≡CCH <sub>2</sub> CH <sub>3</sub>	(CH <sub>2</sub> ) <sub>3</sub> CF <sub>3</sub>
OCH <sub>2</sub> C≡CH	SMe
NH <sub>2</sub>	SBu
NMe <sub>2</sub>	S (0) Me
NHEt	S (O) Bu

S (O) 2Me S (0) 2Bu OMe OBu OCH<sub>2</sub>CF<sub>3</sub> 0(CH<sub>2</sub>)3CF3 CH<sub>2</sub>OMe (CH<sub>2</sub>) <sub>3</sub>OMe СН=СНМе СН=СНСН2СН3 сн=снсн<sub>2</sub>сг<sub>3</sub> CH=CCl2 OCH2CH=CH2  ${\rm CH_2CH_2OMe}$ OCHF<sub>2</sub> C=CH C≡CCH2CH3 OCH2C=CH NH2  $NMe_2$ NHEt 4-morpholinyl pyrrolidinyl piperidinyl Ph PhO 4-Me-Ph 3-CF3-Ph 4-1-Pr-PhO 4-F2HCO-Ph 3-Et-PhO 4-MeO-PhO 4-MeO-Ph

G <sup>2</sup> =S, R <sup>9</sup> =R <sup>10</sup> =Me,	S (O) <sub>2</sub> Bu	R <sup>13</sup>
X=CH, Y=CR <sup>14</sup>	OMe <sup>-</sup>	н
R <sup>14</sup>	OBu	C1
Cl	och <sub>2</sub> cf <sub>3</sub>	Br
Br	O(CH <sub>2</sub> ) <sub>3</sub> CF <sub>3</sub>	F
F	CH <sub>2</sub> OMe	CN
Me .	(CH <sub>2</sub> ) <sub>3</sub> OMe	ОН
Et · · ·	СН=СНМе	Me
ОМе	сн=снсн <sub>2</sub> сн <sub>3</sub>	Hex
OEt	CH=CHCH <sub>2</sub> CF <sub>3</sub>	Et
H	CH=CC1 <sub>2</sub>	i-Pr
•	осн <sub>2</sub> сн <del>-</del> сн <sub>2</sub> .	c-Pr .
$G^2=0$ , Y=N, X=CH,	CH <sub>2</sub> CH <sub>2</sub> OMe	с-неж
R <sup>10</sup> =H	OCHF <sub>2</sub>	2-Me-c-Pr
R <sup>9</sup>	C≡CH	CF <sub>3</sub>
H	C≡CCH <sub>2</sub> CH <sub>3</sub>	(CH <sub>2</sub> ) <sub>3</sub> CF <sub>3</sub>
CI	OCH <sub>2</sub> C≡CH	SMe
Br	NH <sub>2</sub>	SBu ·
F .	NMe <sub>2</sub>	S (0) Me
CN	NHEt	S (O) Bu
ОН	4-morpholinyl	S (O) <sub>2</sub> Me
Me	pyrrolidinyl	S (O) <sub>2</sub> Bu
Hex	piperidinyl	OMe
Et	Ph	OBu
i-Pr	PhO	OCH <sub>2</sub> CF <sub>3</sub>
c-Pr	4-Me-Ph	O(CH <sub>2</sub> )3CF3
c-Hex	3-CF <sub>3</sub> -Ph	CH <sub>2</sub> OMe
2-Me-c-Pr	4-i-Pr-PhO	(CH <sub>2</sub> ) 3 <sup>OMe</sup>
CF <sub>3</sub>	4-F <sub>2</sub> HCO-Ph	CH=CHMe
(CH <sub>2</sub> ) <sub>3</sub> CF <sub>3</sub>	3-Et-PhO	сн=снсн <sub>2</sub> сн <sub>3</sub>
SMe	4-MeO-PhO	CH=CHCH2CF3
SBu	4-MeO-Ph	CH=CCl <sub>2</sub>
S (0) Me		осн <sub>2</sub> сн=сн <sub>2</sub>
S (0) Bu	$G^{2}=0$ , $R^{9}=R^{10}=Me$ ,	CH <sub>2</sub> CH <sub>2</sub> OMe
S (O) 2Me	X=CR <sup>13</sup> , Y=N	OCHF <sub>2</sub>

F	
F .	c-Pr
CN	CF <sub>3</sub>
OFF	SMe
Me	S(0)Me
Et	S (0) 2Me
ř-Pr	OMe
c-Pr	OEt
CF <sub>3</sub>	OCH <sub>2</sub> OMe
SMe	OCH <sub>2</sub> CF <sub>3</sub>
S (0)Me	С=СНМе
S (0) 2Me	C=CMe
OMe.	· NMe <sub>2</sub>
OEt	Ph
OCH <sub>2</sub> OMe	PhO
OCH2CF3	4-Me-Ph
C=CHMe	4-MeO-Ph
C≖CMe	H
NMe <sub>2</sub>	
Ph	$G^2=0$ , $R^9=Me$ , $X=Y=N$
PhO	R <sup>10</sup>
4-Me-Ph	CI
4-MeO-Ph	Br
H.	F
	CN -
G <sup>2</sup> =S, R <sup>9</sup> =Me, Y=CH,	OH
X=N	Me
R <sup>10</sup>	Et
C1	i-Pr
Br	c-Pr
E ·	CF3
CN	SMe .
OH	S (O) Me
Me.	S(O)2Me
Et	OMe
i-Pr	OEt
	CN OH Me Et i-Pr c-Pr C-Pr CF3 SMe S(O)Me S(O)2Me OMe OEt OCH2OMe OCH2CF3 C-CHMe C=CMe NMe2 Ph PhO 4-Me-Ph 4-MeO-Ph H  G <sup>2</sup> =S, R <sup>9</sup> =Me, Y=CH, X=N R <sup>10</sup> Cl Br F CN OH Me Et

	1		1		
OCH <sub>2</sub> OMe		C1	i	OEt	
OCH <sub>2</sub> CF <sub>3</sub>	-	Br		OCH <sub>2</sub> OMe	
C=CHMe	· [	F		OCH <sub>2</sub> CF <sub>3</sub>	
C=CMe	Ì	CIN		C=CHMe	
NMe <sub>2</sub>		ОН		C≕CMe	
Ph ·		Me		NMe <sub>2</sub>	
PhO	İ	Et		.Ph	
4-Me-Ph		1-Pr		PhO	
4-MeO-Ph		c-Pr		4-Me-Ph	
H		CF3		4-MeO-Ph	
		SMe	1	H	
$G^2=0$ , $R^9=Me$	e, Y=CH,	S (0) Me			
X≈N		S (0) <sub>2</sub> Me			
R <sup>10</sup>	2.3	OMe .			
				. *	
G <sup>2</sup> =S			•	•	
<b>X</b>	<b>Y</b> .	R14	R <sup>9</sup>	R13	R <sup>10</sup>
N	CR <sup>14</sup>	-(CH <sub>2</sub> ) <sub>3</sub> -			Me
CH	CR <sup>14</sup>	-(CH <sub>2</sub> ) <sub>3</sub> -			Me
N	CR14	-(CH <sub>2</sub> ) <sub>4</sub> -			Me
CH	CR <sup>14</sup>	-(CH <sub>2</sub> ) <sub>4</sub> -			Me
CR13	N .		-(CH <sub>2</sub> ) <sub>3</sub> -	•	Me
	- CH		-(CH <sub>2</sub> ) <sub>3</sub> -		Me
CR13	и	:	-(CH <sub>2</sub> ) <sub>4</sub> -		Me
CR13	CH		-(CH <sub>2</sub> ) <sub>4</sub> -		Me
CR13	CH		Me	-(CH <sub>2</sub> ) <sub>3</sub> -	
CR <sup>13</sup>	CH		Me	-(CH <sub>2</sub> ) <sub>4</sub> -	
	,			2.1	
G <sup>2</sup> =O					
<b>X</b> .	¥	R14	R <sup>9</sup>	R <sup>13</sup>	R <sup>10</sup>
N .	CR14	-(CH <sub>2</sub> ) <sub>3</sub> -			Me
CH .	CR <sup>14</sup>	-(CH <sub>2</sub> ) <sub>3</sub> -			Me
N	CR <sup>14</sup>	- (CH <sub>2</sub> ) <sub>4</sub> -			Me
СН	CR14	- (CH <sub>2</sub> ) <sub>4</sub> -			Me
CR13	N		-(CH <sub>2</sub> ) <sub>3</sub> -		Me
			_		

CR13	CH		-(CH <sub>2</sub> ) <sub>3</sub> -	Me
CR <sup>13</sup>	n :	· · ·	-(CH <sub>2</sub> ) <sub>4</sub> -	Me
CR13	CH	. <del></del> ·	-(CH <sub>2</sub> ) <sub>4</sub> -	Me
CR13	CH		Me .	-(CH <sub>2</sub> ) <sub>3</sub> -
CR <sup>13</sup>	CH	· ·	Me	- (CH <sub>2</sub> ) 4-

# Compounds of Formula IId

$G^2=S$ , $X=Y=N$ , $R^{11}=R^{12}$	<sub>=R</sub> 28 <sub>=H</sub> .	
R10	c-Pr	С=СНМе
CI	CF3	C≖CMe
Br .	SMe	NMe <sub>2</sub>
F	S (0) Me	Ph .
CN :	S(0)2Me	PhO
OH	OMe	4-Me-Ph
Me .	OEt	4-MeO-Pl
Et .	OCH <sub>2</sub> OMe	H
i-Pr	OCH <sub>2</sub> CF <sub>3</sub>	

G <sup>2</sup> =S, R	10 <sub>-Me</sub>	•			
<b>x</b> .	x	R <sup>11</sup>	R <sup>12</sup>	R <sup>28</sup>	R <sup>31</sup>
CH	N.	H	H	H	H
N	· CH	н .	H	H	H .
N.	N.	н .	3-Me	4-Me .	H
N .	N	H	3-Me	4-Me	6-ме
<b>N</b>	N	Me	H	H	7-Me
N	N	Ħ	<b>H</b> .	4-1-Pr	6-OMe
N.	N	H	3-Me .	H	. 7-CF3
N	N	Ħ	H.	4-Et	7-Et
И.	<b>N</b> .	H:	Ħ	4-1-Pr	6-OCHF2
и .	N	H -	. н .	Ħ	8-Bu
N .	. <b>N</b>	Ħ	H .	4-c-Pr	6-OEt

	X=Y=N, R	1 <sub>-R</sub> 12 <sub>-R</sub> 28 <sub>-</sub>	н		
B <sup>10</sup>		0-	Pr	OCH <sub>2</sub> C	F <sub>3</sub>
Cl		CF	<b>'3</b>	С=СНМ	
Br	**	SM		C≡CMe	
F		s	O) Me	NMe <sub>2</sub>	
CIN		S (	0) <sub>2</sub> Me	Ph	
OH		OM	ie	PhO	· ·
Me .		· OE	t.	4-Me-1	? <b>b</b>
Et		oc	H <sub>2</sub> OMe	4-MeO-	-Ph
i-Pr	. 11	ŀ		н	
G <sup>2</sup> =0,					
x	X	- R11	R12	R <sup>28</sup>	R <sup>31</sup>
CH	N	H	н	н	H
N	ĊН	H	Н	н	H
N	N	H	3-Me	4-Me	H
n	N	H	3-Me	4-Me ·	6-Me
N	N	Me	H	н	7-Me
N	n :	H	H	4-1-Pr	6-OMe
N	·· N	H	3-Me	H	7-CF <sub>3</sub>
N	N '	H.	H	4-Et	. 7-Et
N	N.	H	н	4-1-Pr	6-OCHF <sub>2</sub>
N .	N	H.	H	· H	8-Bu
N	N.	Н	H	4-c-Pr	6-OEt
		•			

	Compounds of Formula IIe	LA .
G <sup>2</sup> =S, R <sup>12</sup> =H, R <sup>28</sup> =H	Br	G <sup>2</sup> =S, R <sup>11</sup> =H, R <sup>28</sup> =H
R <sup>11</sup>	CF <sub>3</sub>	R <sup>12</sup>
н	OMe ·	3-Me
Me	OEt	3-Et
Et	OCHF <sub>2</sub>	3-1-Pr
i-Pr	OBu	3- <i>s</i> -Bu
g-Bu :	O(CH <sub>2</sub> ) <sub>3</sub> CF <sub>3</sub>	3-F
F	(CH <sub>2</sub> ) <sub>3</sub> CF <sub>3</sub>	3-C1
CI		3-Br

		•
3-CF <sub>3</sub>	4-OCH <sub>2</sub> OMe	F .
3-OMe	4-CH <sub>2</sub> OMe	CI .
3-0Et	4-CH=CH-Me	Br
3-0CHF <sub>2</sub>	4-CH=CHCH2Me	CF <sub>3</sub>
3-0Bu	4-TBS	OMe
3-0 (CH <sub>2</sub> ) <sub>3</sub> CF <sub>3</sub>	4-SiMe3	OEt .
3-(CH <sub>2</sub> ) <sub>3</sub> CF <sub>3</sub>	4-C=CH	OCHF <sub>2</sub>
•	4-C≡C-Et	OBu
$G^2=S$ , $R^{11}=R^{12}=H$	4-0CH <sub>2</sub> C≡CH	O(CH <sub>2</sub> ) <sub>3</sub> CF <sub>3</sub>
R <sup>28</sup>	4-NMe <sub>2</sub>	(CH <sub>2</sub> ) <sub>3</sub> CF <sub>3</sub>
4-Me	4-C (=0) NMe <sub>2</sub>	
4-CN	4-Ph	$G^2=0$ , $R^{11}=H$ , $R^{28}=H$
4-NO <sub>2</sub>	4-0Ph	R <sup>12</sup>
4-OH	4-SPh	3-Me
4-co <sub>2</sub> H	4-(3-Me-Ph)	3-Et
4-CO <sub>2</sub> Et		3-1-Pr
4-Et	G <sup>2</sup> =S	3- <i>s</i> -Bu ,
4-i-Pr	R <sup>11</sup> R <sup>12</sup> R <sup>28</sup>	3-F
4-n-Hex	С1 Н 6-С1	3-C1
4-c-Pr	H 3-Me 4-Me	3-Br
4-CF3	H 3-Me 4-Et	3-CF3
4-SMe	H 3-OMe 4-OMe	3-0Me
4-SBu	Me H 5-Me	3-0Et
4-c-Hex	Me H 4-Me	3-0CHF <sub>2</sub>
4-C1	Me 4-Me 5-Me	3-0Bu
4-Br -	H 3-CL 5-Cl	3-0 (CH <sub>2</sub> ) 3CF3
4-F	C1 H 4-C1	3-(CH <sub>2</sub> ) <sub>3</sub> CF <sub>3</sub>
4-(CH <sub>2</sub> ) <sub>3</sub> CF <sub>3</sub>		4-Me
4-S (0) Me	G <sup>2</sup> =0, R <sup>12</sup> =H, R <sup>28</sup> =H	
4-\$ (0) Bu	R <sup>11</sup>	$G^2=0$ , $R^{11}=R^{12}=H$
4-S (O) 2Me	н	R <sup>28</sup>
4-S (0) 2Bu	Ме	4-CN
4-OMe	Et	4-NO <sub>2</sub>
4-0Bu	i-Pr	4-ОН
4-OCH <sub>2</sub> CF <sub>3</sub>	s-Bu	4-CO <sub>2</sub> H

	1			
4-CO <sub>2</sub> Et	}			$G^2=S(0)$ , $R^{11}=H$ ,
4-Et	G <sup>2</sup> =0			R <sup>28</sup> ≕H
4-1-Pr	B <sup>11</sup>	R12	R <sup>28</sup>	R <sup>12</sup>
4-n-Hex	Cl	H	6-C1	3-Me
4-c-Pr	н	3-Me	4-Me	3-Et
4-CF <sub>3</sub>	н	3-Me	4-Et	3-i-Pr
4-SMe	н	3-0Me	4-OMe	3- <i>s</i> -Bu
4-SBu	Me	н	5-Me	3-F
4-c-Hex	Me	H	4-Me ·	3-C1
4-C1	Me	4-Me	5-Me	3-Br
4-Br	н	3-C1	5-C1	3-CF <sub>3</sub>
4-F	Cl	н	4-C1	3-0Me
4-(CH <sub>2</sub> ) <sub>3</sub> CF <sub>3</sub>				3-0Et
4-S (O) Me	G <sup>2</sup> =S (	0), R <sup>12</sup>	=H,	3-0CHF <sub>2</sub>
4-S (0) Bu	R <sup>28</sup> ≕H			3-0Bu
4-S (0) <sub>2</sub> Me	R <sup>11</sup>			3-0 (CH <sub>2</sub> ) 3CF3
4-S (O) 2Bu .	·H			3-(CH <sub>2</sub> ) <sub>3</sub> CF <sub>3</sub>
4-OMe	Me			
4-OBu	Et			$G^2=S(0), R^{11}=R^{12}=H$
4-0CH <sub>2</sub> CF <sub>3</sub>	i-Pr			R <sup>28</sup>
4-OCH <sub>2</sub> OMe	s-Bu			4-Me
4-CH <sub>2</sub> OMe	F			4-CN
4-CH=CH-Me	Cl			4-NO <sub>2</sub>
4-CH=CHCH <sub>2</sub> Me	Br			4-OH
4-TBS	CF <sub>3</sub>			4-CO2H
4-SiMe3	OMe			4-CO <sub>2</sub> Et
4-C≡CH	OEt			4-Et
4-C=C-Et	OCHF <sub>2</sub>			4-i-Pr
4-OCH <sub>2</sub> C≡CH	OBu		İ	4-n-Hex
4-NMe <sub>2</sub>	O (CH <sub>2</sub> )	3CF3	(3)	4-c-Pr
4-C (=0) NMe <sub>2</sub>	(CH <sub>2</sub> ) 3	3CF3		4-CF3
4-Ph			j	4-SMe
4-OPh			ĺ	4-SBu
4-SPh				4-c-Hex
4-(3-Me-Ph)				4-C1

4-Br	н 3-С1 5-С1	3-0CHF <sub>2</sub>
4-F	Cl H 4-CI	3-OBu
4-(CH <sub>2</sub> ) <sub>3</sub> CF <sub>3</sub>		3-0 (CH <sub>2</sub> ) 3CF3
4-S (O) Me	G2=S(O)2, R12=H,	3-(CH <sub>2</sub> ) <sub>3</sub> CF <sub>3</sub>
4-S (O) Bu	R28_H	
4-S (O) 2Me	R <sup>11</sup>	G <sup>2</sup> =S (O) <sub>2</sub> ,
4-S (O) 2Bu	H	R11_R12_H
4-0Me	Me	R <sup>28</sup>
4-0Bu	Et	4-Me
4-0CH <sub>2</sub> CF <sub>3</sub>	i-Pr	4-CN
4-0CH <sub>2</sub> OMe	s-Bu	.4-NO <sub>2</sub>
4-CH <sub>2</sub> OMe	F	4-OH
4-CH=CH-Me	Cl	4-co <sub>2</sub> H
4-CH=CHCH <sub>2</sub> Me	Br	4-00 <sub>2</sub> Et
4-TBS	CF <sub>3</sub>	4-Et
4-SiMe <sub>3</sub>	OMe .	4-i-Pr
4-C≡CH	OEt.	4-n-Hex
4-C≕C-Et	OCHF <sub>2</sub>	4-c-Pr
4-0CH <sub>2</sub> C=CH	OBu	4-CF3
4-NMe <sub>2</sub>	O (CH <sub>2</sub> ) 3CF3	4-SMe
4-C (=0) NMe <sub>2</sub>	(CH <sub>2</sub> ) <sub>3</sub> CF <sub>3</sub>	4-SBu
4-Ph		4-c-Hex
4-0Ph	G <sup>2</sup> =S(O) <sub>2</sub> , R <sup>11</sup> =H,	4-C1
4-SPh	<sub>R</sub> 28 <sub>≠H</sub>	4-Br
4-(3-Me-Ph)	R12	4-F
· 26.	3-Me	4-(CH <sub>2</sub> )3CF3
G <sup>2</sup> =5 (0)	3-Et	4-S(O)Me
R11 R12 R28	3-i-Pr	4-S (0) Bu
C1 H 6-C1	3- <i>s</i> -Bu	4-S (0) 2Me
Н 3-Me 4-Me	3-F	4-5 (0) 2Bu
H 3-Me 4-Et	3-C1	4-0Me
H 3-OMe 4-OMe	3-Br	4-OBu
Me H 5-Me	3-CF3	4-OCH <sub>2</sub> CF <sub>3</sub>
Me H 4-Me	3-0Me	4-OCH <sub>2</sub> OMe
Me 4-Me 5-Me	3-0Et	4-CH <sub>2</sub> OMe

65..

	1	•	
4-CH=CH-Me	CHF <sub>2</sub>	C (=0) Ph	
4-CH=CHCH <sub>2</sub> Me	(CH <sub>2</sub> ) <sub>3</sub> CF <sub>3</sub>	(3-Me-Ph)C(=0)	
4-TBS	CO <sub>2</sub> Et	(4-OMe-Ph)C(=O)	
4-SiMe <sub>3</sub>	C (=0) Me	CH <sub>2</sub> C=CH <sub>2</sub>	
4-C≡CH	C (=0) (CH <sub>2</sub> ) 3Me	сн₂с≡сн	
4-C≡C-Et	C (=0) Ph	PhCH <sub>2</sub>	
4-OCH2C≡CH	(3-Me-Ph)C(=0)	4-Me-PhCH <sub>2</sub>	
4-NMe2	(4-OMe-Ph)C(=O)	S <sub>.</sub> (O) <sub>2</sub> Me	
4-C (=0) NMe <sub>2</sub>	CH2C=CH2	C (=0) NMe2	
4-Ph	CH <sub>2</sub> C≡CH	C (=S) NHMe	
4-OPh	PhCH <sub>2</sub>	S (0) Me	
4-SPh	4-Me-PhCH <sub>2</sub>	S (O) <sub>2</sub> Ph	
4-(3-Me-Ph)	S (O) 2Me	(4-Me-Ph) S (0) 2	
•	C (=0) NMe <sub>2</sub>	C (=O) NHPh	
$G^2=S(O)_2$	C (=S) NHMe	C (=S) NHPh	
R <sup>11</sup> R <sup>12</sup> R <sup>28</sup>	S (0) Me	P (=S) (OEt)2	
C1 H 6-C1	S (O) 2Ph .	P (=0) (OEt) 2	
H 3-Me 4-Me	(4-Me-Ph)S(O)2	S(O) <sub>2</sub> N(Et) <sub>2</sub>	
H 3-Me 4-Et	C (=0) NHPh		
H 3-OMe 4-OMe	C (=S) NHPh	n <sup>1</sup> =3	
Me H 5-Me	P (=S) (OEt) <sub>2</sub>	R <sup>27</sup>	
Me H 4-Me	P (=0) (OEt) <sub>2</sub>	H ·	
Me 4-Me 5-Me	S(0)2N(Et)2	Et	
H 3-C1 5-C1		⊮ <b>Bu</b>	
C1 H 4-C1	n <sup>1</sup> =2	i-Pr	
	R <sup>27</sup>	CHF <sub>2</sub>	
TABLE 14	н .	(CH <sub>2</sub> ) <sub>3</sub> CF <sub>3</sub>	
Compounds of	Et	∞ <sub>2</sub> Et	
Formula IIf	Bu	C (=0) Me	
n <sup>1</sup> =1	i-Pr	C (=0) (CH2) 3Me	
R <sup>27</sup>	CHF <sub>2</sub>	C (=0) Ph	
н .	(CH <sub>2</sub> ) <sub>3</sub> CF <sub>3</sub>	(3-Me-Ph) C (=O)	
Et	CO <sub>2</sub> Et	(3-Me-Ph) C (=O)	
Bu	C (=0) Me	CH <sub>2</sub> C=CH <sub>2</sub>	
i-Pr	C (=0) (CH <sub>2</sub> ) 3Me	сн₂с≡сн	

PhCH <sub>2</sub>						1	: 1		S (O)
4-Me-PhCH <sub>2</sub>			TABL	15		.1	2		S (O)
S (O) 2Me			Compou	nds of	:	2	1		S (O)
C (=0) NMe <sub>2</sub>		1	Formul	_		0	. 3		S (O)
C (=S) NHMe		n	$n^1$	<u>G</u> 2		ī	1		s (0) <sub>2</sub>
S (0) Me		. 1	. 1 .	S		1	2		s(0)2
S (0) 2Ph		1	2.	S.		2	1		s (0) 2
(4-Me-Ph) S (0) 2	•	2	1	S		0	: 3		s (0) <sub>2</sub>
C (=O) NHPh		0	3	S	•	1	1		N-Me
C (=S) NHPh		Ţ	1	. 0		1	2 .	. •	N-Me
P (=S) (OEt) 2		1	2 .	: · o		2	. 1	•	N-Me
P (=0) (OEt) 2		2	1	0					
S (O) 2N (Et) 2		0.	3	. 0				٠.	
TAB	LE 16			1	Me		Me	H	H
Compounds of	Formu	la II	ħ;	1	H		H	Me	. н
G <sup>2</sup> =S				1	H	:	H.	Bu	H
$n^2$ $R^1$	R <sup>7</sup>	R4	R8	1	Ph		, H	Ħ	H.
1 Me	H	H	H.	1	4-Me	e-Ph	H	H	H
1 Bu	H	H	H	1	4-02	le-Ph	. <b>H</b>	H	H
1 Me	Me	H	H·	0	Me		H		
1 H	H	Me .	H.	0	Bu		н		<u>.</u>
1 H	Ħ	Bu	H	. 0	Me	٠.	Me		
1 Ph	H.	H .	Ħ .	0 -	Ph	: ·	H		٠
1 4-Me-Ph	H	H .	H	0	4-M	e-Ph	· н ·		
1 4-OMe-Ph	H	Н -	• н						
0 Me	H				• .	. 72	ABLE 1	2	
0 Bu	Ħ	<b></b> .			Compou	nds .	of For	mula	III .
0 Me	Me	<u></u>	<del></del>	G <sup>2</sup> =		·	٠.,		
0 Ph	H	<del></del>		n <sup>2</sup>	R <sup>1</sup>		R <sup>2</sup>	-	R3
0 4-Me-Ph	H	·		0	Me		Ħ		
				0	Bu	•	Ħ		
G <sup>2</sup> =0				0	н		Me		
n <sup>2</sup> R <sup>1</sup> .	. B <sup>7</sup>	R4	R8	0	Ħ		Bu		
1 Me	H	H	· <b>H</b>	0	<b>Ph</b>		H		
1 Bu .	Ħ	Ħ	H	0	4-Me-1	2h	H		
		•	49.5						

67

				,		•	
0	H	4-OMe-Ph		0	H .	Me	
n	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	0	Н	Bu	
1	Me	Ħ	H	0	Ph ,	н	
1	Bu	H	H	0	4-Me-Ph	Н	
1	н	Me	H	0	н .	4-OMe-Ph	
1	H	Bu .	H	1	Me	н .	H
1	H	н .	Me	. 1	Bu	H	H
1	н .	H.	Bu	1	H.	Me	н
1	Ph	H	н	1	н .	Bú	н .
1	4-Me-Ph	н	H	1	H	H	Me
1	H	Ph	H	1	. н	. н	Bu
1	н .	4-Me-Ph	H	1	Ph	H	н .
1	н .	H	Ph	1	4-Me-Ph	H	н
1	Н	<b>H</b> .	4-Me-Ph	1	H	Ph	H
				1	H	4-Me-Ph	H ·
G <sup>2</sup> -	<b>=</b> 0		*	1	н .	H	Ph
$n^2$	R <sup>1</sup>	R <sup>2</sup>	₽ <sup>3</sup>	· 1	H	H	4-Me-Ph
0	Me	H					
0	Bu .	н			•		

#### TABLE 18

## Compounds of Formula IIj

			100		_		
G <sup>2</sup> =S				H	H	H	4-OMe-Ph
R <sup>1</sup>	R7	<b>R</b> <sup>5</sup>	R <sup>6</sup>	Bu	H	H	H
H	H	Me	н	3-Me-Ph	H	B	H
н	H	Ph	н	4-OMe-Ph	H	H	н
H	H	H	Me	G <sup>2</sup> =0			
H	н	H	Ph	R <sup>1</sup>	R <sup>7</sup>	<b>R</b> <sup>5</sup>	R <sup>6</sup>
Me	H	H	н	H -	H	Me	H
Me	Me	H	н	н .	H	Ph:	H
Ph	H	н	н	н .	н -	B	Me ·
н .	Ph	H	н ,	H	H	H	Ph
<b>H</b> .	H	Bu	H	Me	H	H	<b>H</b> ·
H	н	4-Me-Ph	н	Me	Me	H	H
H	H	н	Bu	Ph	н	H	н

_	O	
O	0	١

					•	
H	Ph	H	н.	H	1-Pr	H
- H	H	Bu	н	2-C1	H	H
H	H	4-Me-Ph	н	3-C1	R	H
H .	Ħ	Ħ	Bu	H	CI	H
H	H	H	4-OMe-Ph	3-Me	Me	Ħ.
Bu	H	H .	H.	2-Me	H .	5-Me
3-Me-Ph	H	· H	н	2-C1	<b>H</b> .	6-C1
4-OMe-Ph	H	н .	H	•		
	•	•		G2=O, MClx	=ZnCl <sub>2</sub>	••
	1	ABLE 19		R <sup>11</sup>	R12	R <sup>28</sup>
Compound	s of	Formula		H	Me	H
<u>G</u> 2		<b>n</b> .	n <sup>1</sup>	н .	Et	H
s		I	1	н	OMe .	·H
S	•	1 .	2	H	i-Pr .	H
s		2 .	. <b>i</b> .	2-C1	H.	Ħ
O .	٠	1	. 1	3-C1	H	Ä
<b>o</b> .		1	2 .	<b>H</b> · .	Cl	H.
o		2 .	, <b>1</b>	. 3-Me	Me ·	H
S (O)		1	. 1	2-Me	H	5-Me
s (O)		1	2	2-C1	H	6-C1
S (Q)		2	· 1			
s(0) <sub>2</sub>		1	1 -	$G_2=S$ , $MCl_{x}$	=FeCl3	
s (0) 2		1	2	R <sup>11</sup>	R <sup>12</sup>	R <sup>28</sup>
S (O) 2		2 .	1	H	Me .	H.
NMe		1 .	1	H	Et	H
NMe		1	. 2 .	Ħ	OMe.	Ħ
NMe		<b>2</b> ·	1	H	i-Pr	H
		•	•	2-CI	Ħ	H
•		TABLE 20	1	3-C1	H	н
Compound	s of	Formula	Im	<b>H</b>	CI	H
G <sub>2</sub> =S, MC		_		3-Me.	Me	H
R11		B <sup>12</sup>	R <sup>28</sup>	2-Me	H :	5-Me
H	:	Me ·	. н	2-C1	Ħ	6-C1
H		Et	<b>H</b>	<b>)</b>	•	
		•				

C -0 MCl -	-EoCl -	1	3-Me	<b>Me</b>	Н
$G_2=0$ , $MCl_{x^c}$	B <sup>12</sup>	R <sup>28</sup> .			
			2-Me	H	5-Me
H.	Me	Н	2-C1	H	6-C1
Н	Et	Н			
Н	OMe	н	G <sub>2</sub> =S, MCl <sub>x</sub>	_	••
н	i-Pr	н	R <sup>11</sup>	R <sup>12</sup>	R <sup>28</sup>
2-C1	H .	н	H	Me	H
3-C1 -	H	H	н	Et	H
н	Cl	H .	н -	OMe	H
3-Me	Me	н .	н	i-Pr	H
2-Me	н	5-Me	2-C1	н	н
2-C1	н	6-C1	3-C1	H	H
			н	ĊŢ	н
G2=S, MClx=	=CuCl <sub>2</sub>		3-Me	Me	н
R <sup>11</sup>	R <sup>12</sup>	R <sup>28</sup> .	2-Me	н	5-Me
н	Me .	H	2-C1	н	6-C1
н	Et	н		. •	
н	OMe .	н .	G2=0, MClx	-MnCl <sub>2</sub>	
H	i-Pr	H .	R <sup>11</sup>	R12	R <sup>28</sup>
2-C1	<b>H</b>	н	н .	Me	H
3-C1	<b>H</b> -	H , ,	н	Et	H .
н .	Cl .	H	н	OMe	н
3-Me.	Me .	H .	H	1-Pr	H
2-Me	н	5-Me	2-C1	н	н
2-C1 .	н	6-C1	3-C1	н	н
	· · · · · · · · · · · · · · · · · · ·		. н	C1	н
G2=O, MClx=	-CuCl <sub>2</sub>		3-Me	Me	н
R <sup>11</sup>	R <sup>12</sup>	R <sup>28</sup>	2-Me	H	5-Me
н	Me	н	2-C1	н	6-C1
н -	Et	н			
H ·	OMe	н	G2=S, MClx=	MgCl <sub>2</sub>	٠.
н .	i-Pr	н .	R <sup>11</sup>	R <sup>12</sup>	R <sup>28</sup>
2-C1	H ·	н	H	Me	н
3-C1	н .	н	н	.Et	н
H	Cl	н	н	OMe .	H
•					

			•		
H	i-Pr	н [	H	Et .	H
2-C1	H	B	н	OMe	H
3-C1	H	н	H	i-Pr	H
H	CI	н .	2-C1	.H	H
3-Me	Me	н	3-C1	H	H
2-Me	H	5-Me	H	CT .	H
2-C1	н	6-C1	. 3-Me	Me	H
			2-Me	H	5-Me
G2=0, MClx=MgCl2		6	2-C1 ·	H	6-C1
R <sup>11</sup>	R <sup>12</sup>	R <sup>28</sup>		•	
H	Me	H		· ·	

### Formulation/Utility

Compounds of this invention will generally be used in formulation with an agriculturally suitable composition. The fungicidal compositions of the present invention comprise an effective amount of at least one compound of Formula I as defined above and at least one of (a) a surfactant, (b) an organic solvent, and (c) at least one solid or liquid diluent. Useful formulations can be prepared in conventional ways. 10 They include dusts, granules, pellets, solutions, suspensions, emulsions, wettable powders, emulsifiable concentrates, dry flowables and the like. Sprayable formulations can be extended in suitable media and used at spray volumes from about one to several hundred 15 liters per hectare. High strength compositions are primarily used as intermediates for further formulation. The formulations will typically contain effective amounts of active ingredient, diluent and surfactant within the following approximate ranges 20 which add up 100 weight percent.

	Weight Percent				
	Active Ingredient	Diluent	Surfactant		
Wettable Powders	25-90	0-74	1-10		
Oil Suspensions, Emulsions, Solutions, (including Emulsifiable Concentrates)	5-50	40-95	0-15		
Dusts	1-25	70-99	0-5		
Granules, Baits and Pellets	0.01-99	5-99.99	0-15		
High Strength Compositions	90-99	0-10	0-2		

Typical solid diluents are described in Watkins, et al., Handbook of Insecticide Dust Diluents and Carriers, 2nd Ed., Dorland Books, Caldwell, New Jersey. Typical liquid diluents and solvents are described in Marsden, Solvents Guide, 2nd Ed., Interscience, New York, 1950. McCutcheon's Detergents and Emulsifiers Annual, Allured Publ. Corp., Ridgewood, New Jersey, as well as Sisely and Wood, Encyclopedia of Surface Active Agents, Chemical Publ. Co., Inc., New York, 1964, list surfactants and recommended uses. All formulations can contain minor amounts of additives to reduce foam, caking, corrosion, microbiological growth, etc.

Methods for formulating such compositions are well
known. Solutions are prepared by simply mixing the
ingredients. Fine solid compositions are made by
blending and, usually, grinding as in a hammer mill or
fluid energy mill. Water-dispersible granules can be
produced be agglomerating a fine powder composition;
see for example, Cross et al., Pesticide Formulations,
Washington, D.C., 1988, pp 251-259. Suspensions are
prepared by wet-milling; see, for example, U.S.
3,060,084. Granules and pellets can be made by

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spraying the active material upon preformed granular carriers or by agglomeration techniques. See Browning, "Agglomeration", Chemical Engineering, December 4, 1967, pp 147-148, Perry's Chemical Engineer's Handbook, 4th Ed., McGraw-Hill, New York, 1963, pp 8-57 and following, and WO 91/13546. Pellets can be prepared as described in U.S. 4,172,714. Water-dispersible and water-soluble granules can be prepared as taught in DE 3,246,493.

For further information regarding the art of 10 formulation, see U.S. 3,235,361, Col. 6, line 16 through Col. 7, line 19 and Examples 10 through 41; U.S. 3,309,192, Col. 5, line 43 through Col. 7, line 62 and Examples 8, 12, 15, 39, 41, 52, 53, 58, 132,

138-140, 162-164, 166, 167 and 169-182; U.S. 15 2,891,855, Col. 3, line 66 through Col. 5, line 17 and Examples 1-4; Klingman, Weed Control as a Science, John Wiley and Sons, Inc., New York, 1961, pp 81-96; and Hance et al., Weed Control Handbook, 8th Ed., Blackwell Scientific Publications, Oxford, 1989.

In the following Examples, all percentages are by weight and all formulations are worked up in conventional ways. Compound numbers refer to Index Table A hereinafter.

25 Example A

#### Wettable Powder

Compound 11	65.0%
dodecylphenol polyethylene glycol ether	2.0%
sodium ligninsulfonate	4.0%
sodium silicoaluminate	6.0%
montmorillonite (calcined)	23.0%.

#### Example B

#### Granule

10.0% Compound 11. attapulgite granules (low volative

	matter, 0.71/0.30 mm; U.S.S. No.	
	25-50 sieves)	90.0%.
	Example C	
	Extruded Pellet	•
5	Compound 11	25.0%
	anhydrous sodium sulfate	10.0%
	crude calcium ligninsulfonate	5.0%
	sodium alkylnaphthalenesulfonate	1.0%
	calcium/magnesium bentonite	59.0%.
10	Example D	
	Emulsifiable Concentrate	
	Compound 11	20.0%
	blend of oil soluble sulfonates	
	and polyoxyethylene ethers	10.0%
15	isophorone	70.0%.
	The compounds of this invention are u	seful as plant
	disease control agents. The present inve	ntion
٠.	therefore further comprises a method for	controlling
	plant diseases caused by fungal plant pat	hogens
20	comprising applying to the plant or porti	on thereof to
	be protected, or to the plant seed or see	dling to be
	protected, an effective amount of a compo	und of Formula
	I or a fungicidal composition containing	said compound.
	The compounds and compositions of this in	3
25	provide control of diseases caused by a b	· · · · · · · · · · · · · · · · · · ·
	of fungal plant pathogens in the Basidiom	
	Ascomycete, Comycete and Deuteromycete cl	· · · · · · · · · · · · · · · · · · ·
	are effective in controlling a broad spec	. <del>-</del>
	diseases, particularly foliar pathogens o	
30	vegetable, field, cereal, and fruit crops	
•	pathogens include Plasmopara viticola, Ph	- · · · · · · · · · · · · · · · · · · ·
	infestans, Peronospora tabacina, Pseudope	<del>-</del>
•	cubensis, Pythium aphanidermatum, Alterna	
2-	Septoria nodorum, Cercosporidium personat	<del>-</del> .
35	arachidicola, Pseudocercosporella herpotr	icnoides,

Cercospora beticola, Botrytis cinerea, Monilinia fructicola, Pyricularia oryzae, Podosphaera leucotricha, Venturia inaequalis, Erysiphe graminis, Uncinula necatur, Puccinia recondita, Puccinia graminis, Hemileia vastatrix, Puccinia striiformis, Puccinia arachidis, Rhizoctonia solani, Sphaerotheca fuliginea, Fusarium oxysporum, Verticillium dahliae, Pythium aphanidermatum, Phytophthora megasperma and other generea and species closely related to these pathogens.

Compounds of this invention can also be mixed with one or more other insecticides, fungicides, nematocides, bactericides, acaricides, semiochemicals, repellants, attractants, pheromones, feeding stimulants or other biologically active compounds to form a multicomponent pesticide giving an even broader spectrum of agricultural protection. Examples of other agricultural protectants with which compounds of this invention can be formulated are: insecticides such as monocrotophos, carbofuran, tetrachlorvinphos, malathion, parathion-methyl, methomyl, chlordimeform, diazinon, deltamethrin, oxamyl, fenvalerate, esfenvalerate, permethrin, profenofos, sulprofos, triflumuron, diflubenzuron, methoprene, buprofezin, thiodicarb, acephate, azinphosmethyl, chlorpyrifos, dimethoate, fipronil, flufenprox, fonophos, isofenphos, methidathion, methamidophos, phosmet, phosphamidon, phosalone, pirimicarb, phorate, terbufos, trichlorfon, methoxychlor, bifenthrin, biphenate, cyfluthrin, fenpropathrin, fluvalinate, flucythrinate, tralomethrin, metaldehyde and rotenone; fungicides such as carbendazím, thiuram, dodine, maneb, chloroneb, benomyl, cymoxanil, fenpropidine, fenpropimorph, triadimefon, captan, thiophanate-methyl, thiabendazole, phosethyl-Al, chlorothalonil, dichloran, metalaxyl, 35

captafol, iprodione, oxadixyl, vinclozolin, kasugamycin, myclobutanil, tebuconazole, difenoconazole, diniconazole, fluquinconazole, ipconazole, metconazole, penconazole, propiconazole, uniconzole, flutriafol, prochloraz, pyrifenox, fenarimol, triadimenol, diclobutrazol, copper oxychloride, furalaxyl, folpet, flusilazol, blasticidin S, diclomezine, edifenphos, isoprothiolane, iprobenfos, mepronil, neo-asozin, pencycuron,

- 10 probenazole, pyroquilon, tricyclazole, validamycin, and flutolanil; nematocides such as aldoxycarb, fenamiphos and fosthietan; bactericides such as oxytetracyline, streptomycin and tribasic copper sulfate; acaricides such as binapacryl, oxythioquinox, chlorobenzilate,
- dicofol, dienochlor, cyhexatin, hexythiazox, amitraz, propargite, tebufenpyrad and fenbutatin oxide; and biological agents such as Bacillus thuringiensis, baculovirus and avermectin B.

In certain instances, combinations with other
fungicides having a similiar spectrum of control but a
different mode of action will be particularly
advantageous for resistance management.

Plant disease control is ordinarily accomplished by

applying an effective amount of a compound of this
invention either pre— or post—infection, to the portion
of the plant to be protected such as the roots, stems,
foliage, fruit, seeds, tubers or bulbs, or to the media
(soil or sand) in which the plants to be protected are
growing. The compounds can also be applied to the seed
to protect the seed and seedling.

Rates of application for these compounds can be influenced by many factors of the environment and should be determined under actual use conditions.

Foliage can normally be protected when treated at a rate of from less than 1 g/ha to 5,000 g/ha of active

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ingredient. Seed and seedlings can normally be protected when seed is treated at a rate of from 0.1 to 10 g per kilogram of seed.

The following Tests demonstrate the control efficacy of compounds of this invention on specific pathogens. The pathogen control protection afforded by the compounds is not limited, however, to these species. See Index Table A for compound descriptions.

Test compounds were first dissolved in acetone in an amount equal to 3% of the final volume and then suspended at a concentration of 200 ppm in purified water containing 250 ppm of the surfactant Trem® 014 (polyhydric alcohol esters). The resulting test suspensions were then used in the following tests.

TEST A

The test suspension was sprayed to the point of run-off on wheat seedlings. The following day the seedlings were inoculated with a spore dust of Erysiphe graminis f. sp. tritici, (the causal agent of wheat powdery mildew) and incubated in a growth chamber at 20°C for 7 days, after which disease ratings were made.

#### TEST B

The test suspension was sprayed to the point of run-off on wheat seedlings. The following day the seedlings were inoculated with a spore suspension of *Puccinia recondita* (the causal agent of wheat leaf rust) and incubated in a saturated atmosphere at 20°C for 24 h, and then moved to a growth chamber at 20°C for 6 days, after which disease ratings were made.

TEST C

The test suspension was sprayed to the point of run-off on rice seedlings. The following day the seedlings were inoculated with a spore suspension of *Pyricularia oryzae* (the causal agent of rice blast) and incubated in a saturated atmosphere at 27°C for 24 h,

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and then moved to a growth chamber at 30°C for 5 days, after which disease ratings were made.

#### TEST D

The test suspension was sprayed to the point of run-off on tomato seedlings. The following day the seedlings were inoculated with a spore suspension of *Phytophthora infestans* (the causal agent of potato and tomato late blight) and incubated in a saturated atmosphere at 20°C for 24 h, and then moved to a growth chamber at 20°C for 5 days, after which disease ratings were made.

#### TEST E

The test suspension was sprayed to the point of run-off on grape seedlings. The following day the seedlings were inoculated with a spore suspension of Plasmopara viticola (the causal agent of grape downy mildew) and incubated in a saturated atmosphere at 20°C for 24 h, moved to a growth chamber at 20°C for 6 days, and then incubated in a saturated atmosphere at 20°C for 24 h, after which disease ratings were made.

#### TEST F

The test suspension was sprayed to the point of run-off on cucumber seedlings. The following day the seedlings were inoculated with a spore suspension of Botrytis cinerea (the causal agent of gray mold on many crops) and incubated in a saturated atmosphere at 20°C for 48 h, and moved to a growth chamber at 20°C for 5 days, after which disease ratings were made.

#### Index Table 1

Compounds of Formula I

$R^{3}=R^{10}=Me;$	X=CH; Y=N	•	•
Cmpd. No.	G1-G2-G3	E	mp (°C)
1 .	CH <sub>2</sub> OCH <sub>2</sub>	Ph	а
2 '	СH <sub>2</sub> CH <sub>2</sub> S	4-Cl-Ph	a

3 .	CH <sub>2</sub> OCH <sub>2</sub>	4-Et-Ph	a.
4 .	CH2CH2O	3-Me-Ph	· a
5	CH <sub>2</sub> CH <sub>2</sub> S	3-Me-Ph	a ·· ·
6	CH <sub>2</sub> CH <sub>2</sub> O	2,6-diCl-Ph	a
7	CH2CH2S	4-Me-Ph	·a
8 ·	CH <sub>2</sub> CH <sub>2</sub> S	2-C1-Ph	146-148
9	CH <sub>2</sub> CH <sub>2</sub> S	3-Cl-Ph	a
10	CH <sub>2</sub> CH <sub>2</sub> O	4-Et-Ph	99-106
11	CH <sub>2</sub> CH <sub>2</sub> S	4-Et-Ph	84-87
12	CH <sub>2</sub> CH <sub>2</sub> SO	2-C1-Ph	168-170
13	CH2CH2S	Ph	142-145
14	CH <sub>2</sub> CH <sub>2</sub> S	3-CF <sub>3</sub> -Ph	105-110
15	CH2CH2S	4-OMe-Ph	111-115
16	CH2CH2SO	4-Et-Ph	149-164
17	CH2CH2SO2	4-Et-Ph	139-141
18	CH <sub>2</sub> CH <sub>2</sub> S	4-t-Bu	114-121
19	CH2CH2CH2S	4-OMe-Ph	119-123
20	CH <sub>2</sub> CH <sub>2</sub> S	OPh .	75-85
21	CH2CH2CH2S	4-Et-Ph	97-100
22	CH (CH <sub>3</sub> ) CH <sub>2</sub> S	4-Et-Ph	. a .
23	CH2CH2S	2-Me-Ph	86-91
24	CH <sub>2</sub> CH <sub>2</sub> S	OBzl	81-93
25	CH <sub>2</sub> CH <sub>2</sub> S	SPh	a
26	CH2CH2S	Bzl	· a.
27	CH2CH2CH2S	Ph	158-160
28	CH (CH <sub>3</sub> ) CH <sub>2</sub> S	Ph	a
29	CH <sub>2</sub> C (CH <sub>3</sub> ) <sub>2</sub> CH <sub>2</sub> S	Ph.	116-121
30	CH <sub>2</sub> CH (Ph) S	Ph	196-208
31	CH2CH2S	Et	a.
32	CH2CH (CO2Et)S	Ph	124-133
33	CH <sub>2</sub> CH (Ph) SO <sub>2</sub>	Ph	201-206
34-	CH (CF3) CH2S	Ph	174-181
35 /	CH (CH <sub>2</sub> CH <sub>3</sub> ) CH <sub>2</sub> S	Ph	a
36	CH <sub>2</sub> CH (CN)S	Ph	208-212
37	CH (CN) CH <sub>2</sub> S	Ph	168-174

Table 2.

79..

38	CH <sub>2</sub> CH <sub>2</sub> S	3,4-diCl-Ph	149-152
39	CH <sub>2</sub> CH <sub>2</sub> S	4-Ph-Ph	151-155
40	CH <sub>2</sub> CH <sub>2</sub> S	3,4-diOMe-Ph	172-174

a Oil or gum; <sup>1</sup>H NMR data in Index Table 2.

X=CR $^{13}$ ; R $^9$  and R $^{13}$  are taken together to form a fused benzene ring; Y=N; R $^{10}$ =Me

Cmpa. No.	G±=G²=G³	E	mp (°C)
38	CH <sub>2</sub> CH <sub>2</sub> S	Ph	102-108
R9=R10=ethy	1; X=CH; :Y=N		:
Cmpd. No.	G <sup>1</sup> -G <sup>2</sup> -G <sup>3</sup>	E	mp (°C)
39	CH <sub>2</sub> CH <sub>2</sub> S	Ph	oil; <sup>1</sup> H NMR data

#### Index Table 2

	THUEX TABLE 2
Cmpd. No.	<sup>1</sup> H NMR Data <sup>a</sup>
1	7.75 (m, 2H), 7.37 (m, 3H), 6.57 (s, 1H),
	5.54 (s, 2H), 4.83 (s, 2H), 2.42 (s, 6H).
· 2	7.83 (d, 2H), 7.35 (d, 2H), 6.56 (s, 1H),
•	4.47 (t, 2H), 3.36 (t, 2H), 2.43 (s, 6H).
3	7.66 (d, 2H), 7.21 (d, 2H), 6.56 (s, 1H),
	5.54 (s, 2H), 4.81 (s, 2H), 2.67 (q, 2H),
-	2.42 (s, 6H), 1.24 (t, 3H).
4	7.82 (m, 1H), 7.75 (m, 1H), 7.25 (m, 1H),
*	7.19 (m, 1H), 6.49 (s, 1H), 4.54 (m, 2H),
٠.	4.28 (m, 2H), 2.42 (s, 6H), 2.38 (s, 3H).
5 .	7.7 (m, 2H), 7.2 (m, 2H), 6.54 (s, 1H),
•	4.45 (m, 2H), 3.35 (m, 2H), 2.42 (s, 6H),
•	2.39 (s, 3H).
6	7.31 (m, 2H), 7.25 (m, 1H), 6.5 (s, 1H),
	4.55 (m, 2H), 4.35 (m, 2H), 2.38 (s, 6H).

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7.77 (d, 2H), 7.18 (d, 2H), 6.53 (s, 1H),
        4.46 (m, 2H), 3.35 (m, 2H), 2.42 (s, 6H),
        2.37 (s. 3H).
        7.90 (m, 1H), 7.75 (m, 1H), 7.3 (m, 2H),
        6.57 (s, 1H), 4.47 (m, 2H), 3.36 (m, 2H),
        2.43 (s, 6H).
        7.82 (d, 2H), 7.22 (d, 2H), 6.52 (s, 1H),
22
        5.7 (m, 1H), 3.45 (d, 1H), 3.00 (d, 1H),
        2.7 (q, 2H), 2.42 (s, 6H), 1.38 (d, 3H),
        1.24 (t, 3H).
        7.65 (m, 2H), 7.34 (m, 3H), 6.55 (s, 1H),
25
        4.40 (m, 2H), 3.25 (m, 2H), 2.41 (s, 6H).
        7.37 (d, 2H), 7.32 (t, 2H), 7.25 (d, 1H),
26
        6.51 (s, 1H), 4.32 (m, 2H), 3.89 (s, 2H),
        3.19 (m, 2H), 2.41 (s, 6H).
        7.93 (d, 2H), 7.37 (m, 3H), 6.54 (s, 1H),
28
        5.7 (m, 1H), 3.45 (d, 1H), 3.02 (m, 1H),
        2.42 (s, 6H), 1.40 (d, 3H).
        6.48 (s, 1H), 4.33 (t, 2H), 3.25 (t, 2H),
31
        2.58 (q, 2H), 2.39 (s, 6H), 1.26 (t, 3H).
       7.85 (d, 2H), 7.37 (m, 3H), 6.52 (s, 1H),
35
        5.50 (m, 1H), 3.38 (d, 1H), 3.20 (d, 1H),
        2.41 (s, 6H), 1.80 (m, 2H), 0.99 (t, 3H).
39
        7.85 (d, 2H), 7.37 (m, 3H), 6.56 (s, 1H),
        4.45 (m, 2H), 3.35 (m, 2H), 2.72 (q, 4H),
        1.31 (t, 6H).
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a 1H NMR data are in ppm downfield from tetramethylsilane. Coupling are designated (s)-singlet, (d)-doublet, (t)-triplet, (q)-quartet, (m)-multiplet. Samples were dissolved in CDCl<sub>3</sub>.

Results for Tests A-F are given in Table A. In the table, a rating of 100 indicates 100% disease control and a rating of 0 indicates no disease control (relative to the controls). NT = Not Tested,

Ψa	hl	0	20

			Table	A		•	
Cmpd No.	Test A	Test B	Test C	Test D	Test E	Test F	
1	98	100	65	23	75	65	
2	76 .	93	99	11	91	2	
3	86*	84*	72*	59*	44	77	
4	73*	64*	73*	36*	0*	32*	
5 -	24*	64*	73*	10*	0*	32*	
6	0* .	0*	29*	0* .	86*	46*	
8	0	80	85	3	100	98	
9	98	100	99	82	92	98	
10	94	100	99	52 ·	85	82	
11	99	100	97	<b>52</b> .	92	98	
12	56	0	0	60	92	0	
13	98	96	91	91	100	· 77	
14	98	82	100	73	100	47	
15	96	98	97	0	i00	98	
16	82	0	0	0	13	0	
17	61	14	0	NT	14	0	
18	82	. 0	86	0	73	83	
19	29	21	57	18	96 ·	99	
20	90	98	99	85	99	99	
21	98	98	94	0	100	69	
22	0	55	91	58	100	0	
23	74	100	94	73	100	. 80	
24	83 -	91	32	63	84	0	
25	90	100	91	63	100	70	
26	92	98	85	70	100	46	
27	55	23	91	14 ·	74	98	
28	56*	96	91	0	100	94	
29	52	80	74	22*	92	94	
30	0.	55	0	22 .	99	66	
31	89	55	0	44	0	66	
32	0	0	0	0	99 .	82	
33	0*	54*	0*	0*	9*	34*	
34	0*	54*	0*	0*	0*	0*	

82 -

38	29	93	97	23	96	0	
39	98	83	91	0.	100	90	

<sup>\*=</sup>Applications of the compound was made at a rate of 40 ppm.

#### What is claimed is:

#### 1. The compounds of Formulae I, II, III and IV,

#### wherein:

 $-G^1-G^2-G^3-$  taken together with the attached atoms 10 form a 5-8 membered ring, wherein  $-G^{1}$  is  $-CR^{1}R^{7}$ -;  $-(CHR^{1}CHR^{2})$ -;  $-(CHR^{1}CHR^{2}CHR^{3})$ -; or -(CHR1CHR2CHR3CHR4)-;  $-G^{2}$ -is -O-; -S-; -S(O)-; -S(O)<sub>2</sub>- or  $-NR^{27}$ -;  $-G^3$ -is  $-CR^4R^8$ -;  $-(CHR^5CHR^6)$ -;  $-(CHR^3CHR^5CHR^6)$ - or a 15 direct bond; X is N or CR<sup>13</sup>; Y is N or CR14; E is H;  $C_1-C_6$  alkyl;  $C_3-C_7$  cycloalkyl optionally substituted with 1-2 methyl; C<sub>1</sub>-C<sub>6</sub> haloalkyl; 20  $C_1-C_6$  alkylthio;  $C_1-C_6$  alkoxy;  $C_1-C_6$  haloalkoxy; or phenyl, phenoxy, phenylthio, phenylamino,

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R31;

phenylmethyl, indanyl, tetrahydronaphthalenyl,
1-naphthalenyl, 2-naphthalenyl, thienyl,
<ul> <li>furanyl or pyridyl each optionally substituted</li> </ul>
with R <sup>11</sup> , R <sup>12</sup> and R <sup>28</sup> ;
$R^1$ , $R^2$ , $R^3$ , $R^4$ , $R^5$ , $R^6$ , $R^7$ and $R^8$ are each
independently H; C1-C4 alky1; C1-C4 haloalky1,
halogen, CO2CH3, CO2CH2CH3, cyano or phenyl
optionally substituted with R <sup>25</sup> ;
provided that
(i) the maximum number of carbon atoms in
$-G^{1}-G^{2}-G^{3}-$ with geminal disubstitution
is one;
(ii) the maximum number of optionally
substituted phenyl substituents on
$-G^{1}-G^{2}-G^{3}-$ is one;
(iii) $-G^3$ — is other than a direct bond in
compounds of Formulae III and IV; and
(iv) $-G^2-G^3$ is other than $-NR^{27}$ in
compounds of Formulae I and II;
$\mathbb{R}^9$ , $\mathbb{R}^{10}$ and $\mathbb{R}^{13}$ are each independently H; halogen;
cyano: hydroxy; C <sub>1</sub> -C <sub>6</sub> alkyl; C <sub>1</sub> -C <sub>4</sub> haloalkyl;
C <sub>1</sub> -C <sub>4</sub> alkylthio; C <sub>1</sub> -C <sub>4</sub> alkylsulfinyl; C <sub>1</sub> -C <sub>4</sub>
alkylsulfonyl; C3-C6 cycloalkyl optionally
substituted with 1-2 methyl groups; C1-C4
alkoxy; $C_1-C_4$ haloalkoxy; $C_2-C_4$ alkoxyalkyl;
C2-C4 alkenyl; C2-C4 haloalkenyl; C2-C4
alkenyloxy; C2-C4 alkynyl; C2-C4 alkynyloxy;
NR <sup>29</sup> R <sup>30</sup> ; or phenyl or phenoxy optionally
substituted with R31; or
R9 and R13 or R10 and R13, or R9 and R14 can be

taken together to form  $-(CH_2)_3-$ ,  $-(CH_2)_4-$  or a fused benzene ring optionally substituted with

	R <sup>11</sup>	, $R^{12}$ , $R^{21}$ , $R^{24}$ , $R^{26}$ and $R^{31}$ are each
		independently halogen; C <sub>1</sub> -C <sub>4</sub> alkyl; C <sub>1</sub> -C <sub>4</sub>
		haloalkyl; C <sub>1</sub> -C <sub>4</sub> alkoxy; or C <sub>1</sub> -C <sub>4</sub> haloalkoxy;
	R <sup>14</sup>	is H; halogen; C <sub>1</sub> -C <sub>2</sub> alkyl; or C <sub>1</sub> -C <sub>2</sub> alkoxy;
5		, $R^{16}$ , $R^{17}$ , $R^{18}$ , $R^{29}$ and $R^{30}$ are each
		independently H or C1-C2 alkyl; or
,	R15	and $R^{16}$ , or $R^{17}$ and $R^{18}$ , or $R^{29}$ and $R^{30}$ can be
	-	taken together along with the nitrogen atom to
		which they are attached to form a
10		4-morpholinyl, pyrrolidinyl or piperidinyl
		ring;
	R <sup>20</sup>	and $R^{27}$ are each independently H; $C_1-C_4$ alkyl;
	•	C <sub>1</sub> -C <sub>4</sub> haloalkyl; C <sub>2</sub> -C <sub>5</sub> alkylcarbonyl; phenyl-
٠		carbonyl optionally substituted with R21; C3-C4
15		alkenyl; C3-C4 alkynyl; phenylmethyl optionally
		substituted with $R^{21}$ on the phenyl ring; $C_1-C_4$
		alkylsulfinyl; C <sub>1</sub> -C <sub>4</sub> alkylsulfonyl; phenyl-
	*	sulfinyl, phenylsulfonyl or phenoxycarbonyl
		each optionally substituted with R21; C2-C4
20		alkoxycarbonyl; C(=0)NR <sup>22</sup> R <sup>23</sup> ; C(=S)NHR <sup>23</sup> ;
	121	$P (=S) (C_1-C_4 \text{ alkoxy})_2; P (=0) (C_1-C_4 \text{ alkoxy})_2; or$
		$S(=0)_2NR^{22}R^{23};$
	R <sup>22</sup>	is H or C <sub>1</sub> -C <sub>3</sub> alkyl;
	R <sup>23</sup>	is C <sub>1</sub> -C <sub>4</sub> alkyl; or phenyl optionally
25	•	substituted with R24; or
	R <sup>22</sup>	and $R^{23}$ can be taken together along with the
.•	* - () - W	nitrogen atom to which they are attached to
	4.2	form a 4-morpholinyl, pyrrolidinyl, piperidiny
		or imidazolyl ring;
30	R <sup>25</sup>	is 1-2 halogen; C <sub>1</sub> -C <sub>4</sub> alkyl; C <sub>1</sub> -C <sub>4</sub> haloalkyl;
	•	C <sub>1</sub> -C <sub>4</sub> alkoxy; C <sub>1</sub> -C <sub>4</sub> haloalkoxy; nitro; cyano or
	•	C <sub>1</sub> -C <sub>4</sub> alkylthio; and
••	R <sup>28</sup>	is halogen; cyano; nitro; hydroxy; hydroxy-
		carbonyl; C <sub>1</sub> -C <sub>6</sub> alkyl; C <sub>3</sub> -C <sub>6</sub> cycloalkyl; C <sub>1</sub> -C <sub>6</sub>
35		haloalkyl; C <sub>1</sub> -C <sub>4</sub> alkylthio; C <sub>1</sub> -C <sub>4</sub> alkyl-

sulfinyI; C<sub>1</sub>-C<sub>4</sub> alkylsulfonyl; (C<sub>1</sub>-C<sub>4</sub> alkyl)<sub>3</sub>silyl; C<sub>2</sub>-C<sub>5</sub> alkylcarbonyl; C<sub>2</sub>-C<sub>4</sub> alkenyl; C<sub>3</sub>-C<sub>4</sub> alkenyloxy; C<sub>2</sub>-C<sub>4</sub> alkynyl; C<sub>3</sub>-C<sub>4</sub> alkynyloxy; C<sub>1</sub>-C<sub>4</sub> alkoxy; C<sub>1</sub>-C<sub>4</sub> haloalkoxy; C<sub>2</sub>-C<sub>4</sub> alkoxyalkyl; C<sub>2</sub>-C<sub>5</sub> alkoxycarbonyl; C<sub>2</sub>-C<sub>4</sub> alkoxyalkoxy; NR<sup>15</sup>R<sup>16</sup>; C(=0)NR<sup>17</sup>R<sup>18</sup>; or phenyl, phenoxy or phenylthio each optionally substituted with R<sup>26</sup>;

#### provided that

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when E is,  $C_1$ - $C_6$  alkylthio,  $C_1$ - $C_6$  alkoxy,  $C_1$ - $C_6$  haloalkoxy, phenoxy, phenylthio or phenylamino, then E may only substitute compounds of Formula

and agriculturally suitable salts and metal complexes thereof.

- 2. The compounds of Claim 1, Formula I, wherein: Y is N;
  - E is phenyl, indanyl, tetrahydronaphthalenyl, 1-naphthalenyl, thienyl, or pyridyl each optionally substituted with R<sup>11</sup>, R<sup>12</sup> and R<sup>28</sup>;
  - R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup> and R<sup>8</sup> are each independently H or methyl;
  - R<sup>11</sup> and R<sup>12</sup> are each independently F, Cl, methyl, trifluoromethyl, methoxy or trifluoromethoxy;

R<sup>13</sup> is H;

- $R^9$  and  $R^{10}$  are each independently halogen;  $C_1-C_4$  alkyl; cyclopropyl;  $C_1-C_4$  haloalkyl; allyl; or  $C_2-C_3$  alkynyl; or
- R<sup>9</sup> and R<sup>13</sup> can be taken together to form a fused benzene ring optionally substituted with R<sup>31</sup>;
  - R<sup>28</sup> is halogen; cyano; C<sub>1</sub>-C<sub>4</sub> alkyl; C<sub>1</sub>-C<sub>4</sub> haloalkyl; allyl; propargyl; C<sub>1</sub>-C<sub>4</sub> alkoxy;

 $C_1-C_4$  haloalkoxy; or phenyl or phenoxy each optionally substituted with  $R^{26}$ ; and  $R^{31}$  is halogen;  $C_1-C_4$  alkyl or  $C_1-C_4$  haloalkyl.

- 3. The compounds of Claim 2, wherein:
  G<sup>2</sup> is 0; S or NR<sup>27</sup>; and
  E is phenyl optionally substituted with R<sup>11</sup>, R<sup>12</sup>
  and R<sup>28</sup>; indanyl or tetrahydronaphthalenyl.
- 4. The compounds of Claim 3, wherein:  $G^2$  is 0; S; NH or N(C<sub>1</sub>-C<sub>4</sub> alkyl); and E is phenyl optionally substituted with  $R^{11}$ ,  $R^{12}$  and  $R^{28}$ .
  - 5. The compound of Claim 1, which is 3-(4,6-dimethyl-2-pyrimidinyl)-3,6-dihydro-5-phenyl-2H-1,3,4-oxadiazine.
- 6. The compound of Claim 1, which is 3-(4,6-dimethyl-2-pyrimidinyl)-5-(4-ethyl-phenyl)-3,6-dihydro-2H-1,3,4-oxadiazine.
  - 7. The compound of Claim 1, which is 2-(2-chlorophenyl)-4-(4,6-dimethyl-2-pyrimidinyl)-5,6-dihydro-4H-1,3,4-thiadiazine.
  - 8. The compound of Claim 1, which is 4-(4,6-dimethyl-2-pyrimidinyl)-2-(4-ethyl-phenyl)-5,6-dihydro-4H-1,3,4-thiadiazine.
- 9. A method of controlling fungus disease in plants
  25 which comprises treating the locus to be protected with
  an effective amount of at least one of the compounds of
  Formulae I, II, III or IV, agriculturally suitable
  salts thereof, agriculturally suitable metal complexes
  thereof, or agricultural compositions containing them;

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5 wherein:

 $^{\rm -G^{\rm 1}-G^{\rm 2}-G^{\rm 3}-}$  taken together with the attached atoms form a 5-8 membered ring, wherein

-G<sup>1</sup>-is -CR<sup>1</sup>R<sup>7</sup>-; -(CHR<sup>1</sup>CHR<sup>2</sup>)-; -(CHR<sup>1</sup>CHR<sup>2</sup>CHR<sup>3</sup>)-; or -(CHR<sup>1</sup>CHR<sup>2</sup>CHR<sup>3</sup>CHR<sup>4</sup>)-;

10  $-G^2$  is -0-; -S-; -S(0)-; -S(0)<sub>2</sub>- or -NR<sup>27</sup>-;

-G<sup>3</sup>- is -CR<sup>4</sup>R<sup>8</sup>;- -(CHR<sup>5</sup>CHR<sup>6</sup>)-; -(CHR<sup>3</sup>CHR<sup>5</sup>CHR<sup>6</sup>)- or a direct bond;

X is N or CR13;

Y is N or CR14;

E is H; C<sub>1</sub>-C<sub>6</sub> alkyl; C<sub>3</sub>-C<sub>7</sub> cycloalkyl optionally substituted with 1-2 methyl; C<sub>1</sub>-C<sub>6</sub> haloalkyl; C<sub>1</sub>-C<sub>6</sub> alkylthio; C<sub>1</sub>-C<sub>6</sub> alkoxy; C<sub>1</sub>-C<sub>6</sub> haloalkoxy; or phenyl, phenoxy, phenylthio, phenylamino, phenylmethyl, indanyl, tetrahydronaphthalenyl, 1-naphthalenyl, 2-naphthalenyl, thienyl, furanyl or pyridyl each optionally substituted with R<sup>11</sup>, R<sup>12</sup> and R<sup>28</sup>;

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$R^{1}$ , $R^{2}$ , $R^{3}$ , $R^{4}$ , $R^{5}$ , $R^{6}$ , $R^{7}$ and $R^{8}$ are each
independently H; $C_1-C_4$ alkyl; $C_1-C_4$ haloalkyl,
halogen, CO <sub>2</sub> CH <sub>3</sub> , CO <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> , cyano, or phenyl
optionally substituted with R <sup>25</sup> ;
provided that
(i) the maximum number of carbon atoms in
$-G^1-G^2-G^3-$ with geminal disubstitution
is one;
(ii) the maximum number of optionally
substituted phenyl substituents on
$-G^{1}-G^{2}-G^{3}-$ is one;
(iii) $-G^3$ is other than a direct bond in
compounds of Formulae III and IV; and
(iv) $-G^2-G^3$ is other than $-NR^{27}$ in compounds
of Formulae I and II;
$R^9$ , $R^{10}$ and $R^{13}$ are each independently H; halogen;
cyano; hydroxy; C <sub>1</sub> -C <sub>6</sub> alkyl; C <sub>1</sub> -C <sub>4</sub> haloalkyl;
C <sub>1</sub> -C <sub>4</sub> alkylthio; C <sub>1</sub> -C <sub>4</sub> alkylsulfinyl; C <sub>1</sub> -C <sub>4</sub>
alkylsulfonyl; C3-C6 cycloalkyl optionally
substituted with 1-2 methyl groups; $C_1$ - $C_4$
alkoxy; $C_1-C_4$ haloalkoxy; $C_2-C_4$ alkoxyalkyl;
$C_2-C_4$ alkenyl; $C_2-C_4$ haloalkenyl; $C_2-C_4$
alkenyloxy; C2-C4 alkynyl; C2-C4 alkynyloxy;
NR <sup>29</sup> R <sup>30</sup> ; or phenyl or phenoxy optionally
substituted with R31; or
$\mathbb{R}^9$ and $\mathbb{R}^{13}$ , or $\mathbb{R}^{10}$ and $\mathbb{R}^{13}$ , or $\mathbb{R}^9$ and $\mathbb{R}^{14}$ can be
taken together to form $-(CH_2)_3$ -, $-(CH_2)_4$ - or a
fused benzene ring optionally substituted with
R <sup>31</sup> ;
$R^{11}$ , $R^{12}$ , $R^{21}$ , $R^{24}$ , $R^{26}$ and $R^{31}$ are each
independently halogen; $C_1-C_4$ alkyl; $C_1-C_4$
haloalkyl; C <sub>1</sub> -C <sub>4</sub> alkoxy; or C <sub>1</sub> -C <sub>4</sub> haloalkoxy;

 $R^{14}$  is H; halogen;  $C_1-C_2$  alkyl; or  $C_1-C_2$  alkoxy;

 $R^{15}$ ,  $R^{16}$ ,  $R^{17}$ ,  $R^{18}$ ,  $R^{29}$  and  $R^{30}$  are each independently H or  $C_1$ - $C_2$  alkyl; or

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R15	and $R^{16}$ , or $R^{17}$ and $R^{18}$ , or $R^{29}$ and $R^{30}$ can be
	taken together along with the nitrogen atom to
٠.	which they are attached to form a 4-morpho-
	linyl, pyrrolidinyl or piperidinyl ring;
D20	and D27 and anch independently U. C. C. alberte

R<sup>20</sup> and R<sup>27</sup> are each independently H; C<sub>1</sub>-C<sub>4</sub> alkyl; C<sub>1</sub>-C<sub>4</sub> haloalkyl; C<sub>2</sub>-C<sub>5</sub> alkylcarbonyl; phenyl-carbonyl optionally substituted with R<sup>21</sup>; C<sub>3</sub>-C<sub>4</sub> alkenyl; C<sub>3</sub>-C<sub>4</sub> alkynyl; phenylmethyl optionally substituted with R<sup>21</sup> on the phenyl ring; C<sub>1</sub>-C<sub>4</sub> alkylsulfinyl; C<sub>1</sub>-C<sub>4</sub> alkylsulfonyl; phenyl-sulfinyl, phenylsulfonyl or phenoxycarbonyl each optionally substituted with R<sup>21</sup>; C<sub>2</sub>-C<sub>4</sub> alkoxycarbonyl; C(=0)NR<sup>22</sup>R<sup>23</sup>; C(=S)NHR<sup>23</sup>; P(=S)(C<sub>1</sub>-C<sub>4</sub> alkoxy)<sub>2</sub>; P(=O)(C<sub>1</sub>-C<sub>4</sub> alkoxy)<sub>2</sub>; or S(=O)<sub>2</sub>NR<sup>22</sup>R<sup>23</sup>;

 $R^{22}$  is H or  $C_1$ - $C_3$  alkyl;

 $R^{23}$  is  $C_1-C_4$  alkyl; or phenyl optionally substituted with  $R^{24}$ ; or

R<sup>22</sup> and R<sup>23</sup> can be taken together along with the nitrogen atom to which they are attached to form a 4-morpholinyl, pyrrolidinyl, piperidinyl or imidazolyl ring;

 $R^{25}$  is 1-2 halogen;  $C_1$ - $C_4$  alkyl;  $C_1$ - $C_4$  haloalkyl;  $C_1$ - $C_4$  alkoxy;  $C_1$ - $C_4$  haloalkoxy; nitro; cyano or  $C_1$ - $C_4$  alkylthio; and

R<sup>28</sup> is halogen; cyano; nitro; hydroxy; hydroxy-carbonyl; C<sub>1</sub>-C<sub>6</sub> alkyl; C<sub>3</sub>-C<sub>6</sub> cycloalkyl; C<sub>1</sub>-C<sub>6</sub> haloalkyl; C<sub>1</sub>-C<sub>4</sub> alkylthio; C<sub>1</sub>-C<sub>4</sub> alkyl-sulfinyl; C<sub>1</sub>-C<sub>4</sub> alkylsulfonyl; (C<sub>1</sub>-C<sub>4</sub> alkyl)<sub>3</sub>silyl; C<sub>2</sub>-C<sub>5</sub> alkylcarbonyl; C<sub>2</sub>-C<sub>4</sub> alkenyl; C<sub>3</sub>-C<sub>4</sub> alkenyloxy; C<sub>2</sub>-C<sub>4</sub> alkynyl; C<sub>3</sub>-C<sub>4</sub> alkynyloxy; C<sub>1</sub>-C<sub>4</sub> alkoxy; C<sub>1</sub>-C<sub>4</sub> haloalkoxy; C<sub>2</sub>-C<sub>4</sub> alkoxyalkyl; C<sub>2</sub>-C<sub>5</sub> alkoxycarbonyl; C<sub>2</sub>-C<sub>4</sub> alkoxyalkoxy; NR<sup>15</sup>R<sup>16</sup>; C(=0)NR<sup>17</sup>R<sup>18</sup>; or phenyl,

phenoxy or phenylthio each optionally substituted with  $\mathbb{R}^{26}$ .

#### provided that

when E is,  $C_1-C_6$  alkylthio,  $C_1-C_6$  alkoxy,  $C_1-C_6$  haloalkoxy, phenoxy, phenylthio or phenylamino, then E may only substitute compounds of Formula I.

10. A fungicidal composition comprising a fungicidally effective amount of a compound of 10 Formula I, II, III or IV

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wherein:

-G1-G2-G3- taken together with the attached atoms form a 5-8 membered ring, wherein
-G1- is -CR1R7-; -(CHR1CHR2)-; -(CHR1CHR2CHR3)-; or
-CHR1CHR2CHR3CHR4)-;
-G2-is -O-; -S-; -S(O)-; -S(O)2- or -NR27-;

**35** .

	$-G^3-is$ $-CR^4R^8-$ ; $-(CHR^5CHR^6)-$ ; $-(CHR^3CHR^5CHR^6)-$ or a
	direct bond;
	X is N or CR <sup>13</sup> ;
	Y is N or CR <sup>14</sup> ;
5	E is H; C1-C6 alkyl; C3-C7 cycloalkyl optionally
	substituted with 1-2 methyl; C1-C6 haloalkyl;
	C <sub>1</sub> -C <sub>6</sub> alkylthio; C <sub>1</sub> -C <sub>6</sub> alkoxy; C <sub>1</sub> -C <sub>6</sub> haloalkoxy;
	or phenyl, phenoxy, phenylthio, phenylamino,
	phenylmethyl, indanyl, tetrahydronaphthalenyl,
10	I-naphthalenyl, 2-naphthalenyl, thienyl,
	furanyl or pyridyl each optionally substituted
	with $R^{11}$ , $R^{12}$ and $R^{28}$ .
	$R^1$ , $R^2$ , $R^3$ , $R^4$ , $R^5$ , $R^6$ , $R^7$ and $R^8$ are each
	independently H; C <sub>1</sub> -C <sub>4</sub> alkyl; C <sub>1</sub> -C <sub>4</sub> haloalkyl,
15	halogen, CO <sub>2</sub> CH <sub>3</sub> , CO <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> , cyano or phenyl
10	optionally substituted with R <sup>25</sup> ;
	provided that
	(i) the maximum number of carbon atoms in
	$-G^{1}-G^{2}-G^{3}$ with geminal disubstitution
20	is one:
~ ·	(ii) the maximum number of optionally
	substituted phenyl substituents on
	$-G^1-G^2-G^3$ — is one;
•	(iii) -G <sup>3</sup> - is other than a direct bond in
25	compounds of Formulae III and IV; and
20	(iv) $-G^2-G^3$ is other than $-NR^{27}$ in
•	compounds of Formulae I and II;
	$R^9$ , $R^{10}$ and $R^{13}$ are each independently H; halogen;
	cyano; hydroxy; C <sub>1</sub> -C <sub>6</sub> alkyl; C <sub>1</sub> -C <sub>4</sub> haloalkyl;
30	C <sub>1</sub> -C <sub>4</sub> alkylthio; C <sub>1</sub> -C <sub>4</sub> alkylsulfinyl; C <sub>1</sub> -C <sub>4</sub>
	alkylsulfonyl; C <sub>3</sub> -C <sub>6</sub> cycloalkyl optionally
	substituted with 1-2 methyl groups; C <sub>1</sub> -C <sub>4</sub>
	alkoxy; C <sub>1</sub> -C <sub>4</sub> haloalkoxy; C <sub>2</sub> -C <sub>4</sub> alkoxyalkyl;
-	C-C planula C-C haloalkonula C-C

alkenyloxy; C<sub>2</sub>-C<sub>4</sub> alkynyl; C<sub>2</sub>-C<sub>4</sub> alkynyloxy;

	NR <sup>29</sup> R <sup>30</sup> ; or phenyl or phenoxy optionally
	substituted with R31; or
	$\mathbb{R}^9$ and $\mathbb{R}^{13}$ , or $\mathbb{R}^{10}$ and $\mathbb{R}^{13}$ , or $\mathbb{R}^9$ and $\mathbb{R}^{14}$ can be
	taken together to form $-(CH_2)_3-$ , $-(CH_2)_4-$ or a
5	fused benzene ring optionally substituted with
•	R <sup>31</sup> ;
	$R^{11}$ , $R^{12}$ , $R^{21}$ , $R^{24}$ , $R^{26}$ and $R^{31}$ are each
	independently halogen; C <sub>1</sub> -C <sub>4</sub> alkyl; C <sub>1</sub> -C <sub>4</sub>
	haloalkyl; $C_1-C_4$ alkoxy; or $C_1-C_4$ haloalkoxy;
10	R <sup>14</sup> is H; halogen; C <sub>1</sub> -C <sub>2</sub> alkyl; or C <sub>1</sub> -C <sub>2</sub> alkoxy;
	$R^{15}$ , $R^{16}$ , $R^{17}$ , $R^{18}$ , $R^{29}$ and $R^{30}$ are each
•	independently H or C <sub>1</sub> -C <sub>2</sub> alkyl; or
	$R^{15}$ and $R^{16}$ , or $R^{17}$ and $R^{18}$ , or $R^{29}$ and $R^{30}$ can be
	taken together along with the nitrogen atom to
15	which they are attached to form a
•	4-morpholinyl, pyrrolidinyl or piperidinyl
	ring;
	$R^{20}$ and $R^{27}$ are each independently H; $C_1$ - $C_4$ alkyl;
	C <sub>1</sub> -C <sub>4</sub> haloalkyl; C <sub>2</sub> -C <sub>5</sub> alkylcarbonyl; phenyl-
20	carbonyl optionally substituted with R21; C3-C4
	alkenyl; C3-C4 alkynyl; phenylmethyl optionally
	substituted with $R^{21}$ on the phenyl ring; $C_1-C_4$
	alkylsulfinyl; C <sub>1</sub> -C <sub>4</sub> alkylsulfonyl; phenyl-
	sulfinyl, phenylsulfonyl or phenoxycarbonyl
25	each optionally substituted with R21; C2-C4
	alkoxycarbonyl; $C(=0)NR^{22}R^{23}$ ; $C(=S)NHR^{23}$ ;
	$P(=S) (C_1-C_4 \text{ alkoxy})_2; P(=0) (C_1-C_4 \text{ alkoxy})_2; or$
	S (=O) 2NR <sup>22</sup> R <sup>23</sup> ;
	R <sup>22</sup> is H or C <sub>1</sub> -C <sub>3</sub> alkyl;
30	R <sup>23</sup> is C <sub>1</sub> -C <sub>4</sub> alkyl; or phenyl optionally
	substituted with R <sup>24</sup> ; or
•	${\bf R^{22}}$ and ${\bf R^{23}}$ can be taken together along with the
•	nitrogen atom to which they are attached to
	form a 4-morpholinyl, pyrrolidinyl, piperidinyl
35	or imidazolyl ring;

10

 $R^{25}$  is 1-2 halogen;  $C_1-C_4$  alkyl;  $C_1-C_4$  haloalkyl;  $C_1-C_4$  alkoxy;  $C_1-C_4$  haloalkoxy; nitro; cyano or  $C_1-C_4$  alkylthio; and

R<sup>28</sup> is halogen; cyano; nitro; hydroxy; hydroxycarbonyl; C<sub>1</sub>-C<sub>6</sub> alkyl; C<sub>3</sub>-C<sub>6</sub> cycloalkyl; C<sub>1</sub>-C<sub>6</sub>
haloalkyl; C<sub>1</sub>-C<sub>4</sub> alkylthio; C<sub>1</sub>-C<sub>4</sub> alkylsulfinyl; C<sub>1</sub>-C<sub>4</sub> alkylsulfonyl; (C<sub>1</sub>-C<sub>4</sub>
alkyl)<sub>3</sub>silyl; C<sub>2</sub>-C<sub>5</sub> alkylcarbonyl; C<sub>2</sub>-C<sub>4</sub>
alkenyl; C<sub>3</sub>-C<sub>4</sub> alkenyloxy; C<sub>2</sub>-C<sub>4</sub> alkynyl; C<sub>3</sub>-C<sub>4</sub>
alkynyloxy; C<sub>1</sub>-C<sub>4</sub> alkoxy; C<sub>1</sub>-C<sub>4</sub> haloalkoxy;
C<sub>2</sub>-C<sub>4</sub> alkoxyalkyl; C<sub>2</sub>-C<sub>5</sub> alkoxycarbonyl; C<sub>2</sub>-C<sub>4</sub>
alkoxyalkoxy; NR<sup>15</sup>R<sup>16</sup>; C(=0)NR<sup>17</sup>R<sup>18</sup>; or phenyl,
phenoxy or phenylthic each optionally
substituted with R<sup>26</sup>;

15 provided that

when E is, C<sub>1</sub>-C<sub>6</sub> alkylthio, C<sub>1</sub>-C<sub>6</sub> alkoxy, C<sub>1</sub>-C<sub>6</sub> haloalkoxy, phenoxy, phenylthio or phenylamino, then E may only substitute compounds of Formula I;

and agriculturally suitable salts and metal complexes thereof and at least one of (a) a surfactant, (b) an organic solvent and (c) at least one solid or liquid diluent.

## INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 93/03583

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V. CERTIF	FICATION	,			
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International application No.

#### INTERNATIONAL SEARCH REPORT

PCT/US 93/03583

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)
This international search report has not been established in respect of certain claims under Article 17(2)(2) for the following reasons:
1. Claims Nos.: because they relate to subject matter not required to be searched by this Authority, namely.
<ol> <li>Claims Nos.:         because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:</li> </ol>
•
3. Claims Nos.: because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).
Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)
This International Searching Authority found multiple inventions in this international application, as follows:
1. As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. As all searchable claims could be searches without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:
Remark on Protest  The additional search fees were accompanied by the applicant's protest.  No protest accompanied the payment of additional search fees.
Form PCT/ISA/210 (continuation of first sheet (1)) (July 1992)

International Application No. PCT/US93/03583

#### **FURTHER INFORMATION CONTINUED FROM PCT/ISA**

The definition of the following substituent(s) is too general and/or encompasses too broad a range of totally different chemical groups, only partly supported by examples given in the descriptive part of the application:

X, Y, G1, G2, G3, E

The number of theoretically conceivable compounds resulting from the combination of all claimed substituents of above list precludes a comprehensive search. Guided by the spirit of the application and the inventive concept as disclosed in the descriptive part of the present application the search has been limited to the following case(s):

4-(2-Pyridyl or 2-Pyrimidyl or 2-Triazinyl)-1,3,4-0xa/thiadiazines

4-(2-Pyridyl or 2-Pyrimidyl or 2-Triazinyl)-1,3,4-0xa/thiadiazepines

4-(2-Pyridyl or 2-Pyrimidyl or 2-Triazinyl)-1,3,4-Oxa/thiadiazocines

# ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO.

US 9303583 SA 73324

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.

The members are as contained in the European Patent Office EDP file on

The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

13/07/93

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For more details about this annex: see Official Journal of the European Patent Office, No. 12/82

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